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## CONTENTS

Results of Lysimeter Experiments. A. DEMOLON AND E. BASTISSE .....	1
The Leaching Action of Rain Water upon Dolomite and Limestone Separates Incorporated with Quartz in Outdoor Lysimeters. W. H. MACINTIRE, W. M. SHAW, AND BROOKS ROBINSON .....	9
An Efficient and Convenient Type of Cooling and Freezing Bath. GEORGE JOHN BOUYOUCOS .....	21
The Laterites of Western Samoa. F. T. SEELYE, L. I. GRANGE, AND L. H. DAVIS .....	23
Ferromanganiferous Concretions from Some Podzolic Soils. ERIC WINTERS .....	33
The Presence of Titania in Chemically Unweathered Soils. ANTTI SALMINEN .....	41
Isohydic pH Value of Soils and Its Determination. AMAR NATH PURI AND ANAND SARUP .....	49
Microbial Activities in Soil: IV. Microflora of Different Zonal Soil Types Developed under Similar Climatic Conditions. S. C. VANDECAVEYE AND H. KATZNELSON ..	57
Book Reviews .....	75
Studies on the Behavior of Manganese in Soils. A. L. PRINCE AND S. J. TOTH .....	83
The Movement of Water in Heavy Soils after Irrigation. E. C. CHILDS .....	95
A Field Outfit for Determining the Moisture Content of Soils. GEORGE JOHN BOUYOUCOS .....	107
Hydrogen-Ion Activity of Colloidal Acids in Soils. AMAR NATH PURI AND A. N. DUA ..	113
On the Formation of Structure in Soil: IV. The Structure of Mixed Clay-Sand and Clay-Humus Formations. D. I. SIDERI .....	129
Microbial Activities in Soil: V. Microbial Activity and Organic Matter Transformation in Palouse and Helmer Soils. S. C. VANDECAVEYE AND H. KATZNELSON .....	139
Book Reviews .....	169
Cation Equilibria in Plants in Relation to the Soil. TH. B. VAN ITALLIE .....	175
Fertilization in its Relationship to the Course of Nutrient Absorption by Plants. TH. REMY .....	187
An Evaluation of the Neubauer and the Cunninghamella and Aspergillus Niger Methods for the Determination of the Fertilizer Needs of a Soil. C. A. MOOERS .....	211
Behavior of Calcium, Magnesium, and Potassium Sulfates, as Influenced by Limestone and by Dolomite—A Lysimeter Study. W. H. MACINTIRE, W. M. SHAW, J. B. YOUNG, AND BROOKS ROBINSON .....	229
Influence of Salts and Soil-Water Ratio on pH Value of Soils. AMAR NATH PURI AND A. G. ASGHAR .....	249
A Theory Explaining the Relation of Soil-Water Ratios to pH Values. CLARK M. KEATON .....	259
On the Formation of Structure in Soil: V. Granular Structure. D. I. SIDERI .....	267
The Effect of Sheep and Goat Manure on Some Mediterranean Red Soils. M. PUFFELES AND S. ADLER .....	273
Economical Uses of Fertilizer Elements by Certain Forage Crops. BASIL E. GILBERT AND FREDERICK R. PEMBER .....	279
Effect of "Alkali" Salts on General Microbial Function in Soil. WALTER B. BOLLEN AND SADEGH M. AHI .....	287
Further Studies of Bacterium globiforme and the Incidence of This Type of Organism in Canadian Soils. C. B. TAYLOR .....	307
Oxidation-Reduction Potentials in Soils. AMAR NATH PURI AND ANAND SARUP .....	323

A Mechanical Device for Determining the Permanent Wilting Point of Soils by Means of the Cohesion Method. GEORGE JOEN BOUYOUCOS.....	331
On the Formation of Structure in Soil: VI. Method of Microscopic Investigation of Soil Structure in Reflected Light. D. I. SIDERI.....	337
The Influence of Environmental Factors on Numbers of Soil Microorganisms. W. G. E. EGGLETON.....	351
The Effect of Moisture Changes on Soil as a Medium for Bacterial Growth. H. J. CONN AND MARY A. DARROW.....	365
The Chemical Composition of Soil from Cultivated Land and from Land Abandoned to Grass and Weeds. A. L. PRINCE, S. J. TOOTH, AND A. W. BLAIR.....	379
Action of Hydrogen Peroxide on Weathered Mica. M. DROSDOFF AND E. F. MILES... ..	391
Rapid Determination of Organic Carbon in Soil. E. M. EMMERT.....	397
Interaction Between Carbonates and Soils. AMAR NATH PURI AND M. L. PURI.....	401
Organic Phosphates: I. Fixation Studies with Three Different Soil Types. G. E. HILBERT, L. A. PINCK, M. S. SHERMAN, AND T. H. TREMEARNE.....	409
Book Reviews .....	419
Observations Regarding Soils of Northern and Central Mexico. JOHN T. MILLER AND IRVIN C. BROWN.....	427
The Movement and Fixation of Superphosphate in Soils. B. E. BEATER.....	453
Action of Carbon Dioxide on Soils. A. N. PURI AND H. L. UPPAL .....	467
Coenzyme R. Requirements of Rhizobia. F. E. ALLISON AND F. W. MINOR.....	473
Book Reviews .....	485
Index.....	495

## ILLUSTRATIONS

### PLATES

#### A FIELD OUTFIT FOR DETERMINING THE MOISTURE CONTENT OF SOILS

Plate 1.	Field Outfit for Determining Moisture Content of Soils by the Burning-Alcohol Method.....	111
Fig.	1. Open view of the box with glass windows.....	111
	2. Closed view of box.....	111

#### ON THE FORMATION OF STRUCTURE IN SOIL: IV. THE STRUCTURE OF MIXED CLAY-SAND AND CLAY-HUMUS FORMATIONS

Plate 4.	The Structure of Clay and of Clay-Sand and Clay-Humus Mixtures.....	137
Fig.	1. Clay-sand mixture.....	137
	2. Clay-humus mixture.....	137
	3. Clay "Toida" after treatment with Tamm's reagent.....	137
	4. Clay "Toida" before treatment with Tamm's reagent.....	137

#### ON THE FORMATION OF STRUCTURE IN SOIL: V. GRANULAR STRUCTURE

Plate 1.	Disintegration of the Sand-Clay-Humus Mixture.....	271
----------	--	-----

#### FURTHER STUDIES OF BACTERIUM GLOBIFORME AND THE INCIDENCE OF THIS TYPE OF ORGANISM IN CANADIAN SOILS

Plate 1.	Cultures of <i>Bacterium globiforme</i> Conn.....	321
Fig.	1. <i>Bacterium globiforme</i> Conn, 12-hour culture on beef-peptone agar at 28°C., gentian violet stain, showing rod stage.....	321
	2. <i>Bacterium globiforme</i> Conn, 48-hour culture on beef-peptone agar at 37°C., gentian violet stain, showing bulbous rods.....	321
	3. <i>Bacterium globiforme</i> Conn, 48-hour cultures in nutrient broth at 28°C., gentian violet stain, showing branched forms.....	321
	4. <i>Bacterium globiforme</i> Conn, 48-hour cultures in nutrient broth at 28°C., gentian violet stain, showing branched forms.....	321
	5. <i>Bacterium globiforme</i> Conn, 2-week culture on synthetic medium containing dextrose and cystine, gentian violet stain.....	321
	6. <i>Bacterium globiforme</i> Conn, 2-week cultures on synthetic medium containing dextrose and NaNO <sub>3</sub> , gentian violet stain, showing oval yeast-like cells.....	321
	7. <i>Bacterium globiforme</i> Conn, 2-week cultures on synthetic medium containing xylose and NaNO <sub>3</sub> , gentian violet stain, showing deeply staining bodies.....	321

#### A MECHANICAL DEVICE FOR DETERMINING THE PERMANENT WILTING POINT OF SOILS BY MEANS OF THE COHESION METHOD

Plate 1.	Base, Roller, Pile of Soil before Being Pressed and after Being Pressed, and Pressed Soil Lifted by Roller.....	335
----------	---	-----

ON THE FORMATION OF STRUCTURE IN SOIL: VI. METHOD OF MICROSCOPIC  
INVESTIGATION OF SOIL STRUCTURE IN REFLECTED LIGHT

Plate 5. Fig.	1. The polished clay section "volkonskonite" .....	347
	2. The structure of lamina of desiccated gel (Na-clay "Toida") .....	347
	3. The polished section of "red clay" .....	347
	4. Cross section of the clay lamina ("Toida") and the adhesive material (Na-peat humate) .....	347
	5. Watertight aggregate of the granular structure of weakly leached chernozem .....	347
	6. Watertight columnar alkali soil. ....	347
	7. Watertight aggregate of a podzol soil .....	347
	8. The plowed layer of the soil from the Kuznetzk Experiment Station ..	347
	9. The underlying layer of the soil shown in figure 8 .....	347
	10. The chernozem soil (Kamennaya steppe) saturated with sodium and slightly washed with water .....	347
	11. The soil shown in figure 10, between Nicol prisms .....	347
	12. The columnar alkali soil from Volchia River. The vertical section ..	347
	13. The soil shown in figure 12. The horizontal section .....	347
	14. The soil shown in figure 12, between Nicol prisms .....	347
Plate 6. Fig.	1. The serozem soil from the Ak-Kawak Experiment Station .....	349
	2. The soil shown in figure 1, treated with the products of autolysis of <i>Aspergillus niger</i> .....	349
	3. The Plavsky chernozem soil .....	349
	4. The Plavsky chernozem covered with a thin layer of autolytic prod- ucts of <i>Aspergillus niger</i> .....	349
	5. The Plavsky chernozem covered with a thick layer of autolytic prod- ucts of <i>Aspergillus niger</i> .....	349
	6. The chernozem soil of Suma Agricultural Experiment Station .....	349
	7. The soil shown in figure 6. With 52 tons of manure .....	349
	8. The soil shown in figure 6. With mineral fertilizers .....	349
	9. The soil shown in figure 6. With 52 tons of manure in a pea-sugar beet crop rotation .....	349

ACTION OF HYDROGEN PEROXIDE ON WEATHERED MICA

Plate 1. Mica Particles in Water Compared with Similar Particles in 6 per cent Hydro- gen Peroxide Solution .....	395
--	-----

OBSERVATIONS REGARDING SOILS OF NORTHERN AND CENTRAL MEXICO

Plate 1. Some Soils of Mexico .....	451
Fig. 1. Chernozem profile in excavation south of Irapuato, Guanajuato, showing the unusual depth of the dark colored soil .....	451
2. Cultivated fields on steep slopes in the laterite soils region south of Tamazunchale, Potosi .....	451
3. Profile of a laterite soil south of Tamazunchale, Potosi, showing the steep slopes on which the laterite soils are developed, and also the dense forest in this region .....	451
4. Profile showing unusually deep organic A <sub>1</sub> horizon at an elevation of approximately 13,000 feet on Navado de Toluca .....	451

TEXT-FIGURES

AN EFFICIENT AND CONVENIENT TYPE OF COOLING AND FREEZING BATH

Fig. 1. An Efficient Cooling Bath Used in Connection with the Dilatometer Method and in Freezing-Point Determinations .....	22
--	----

## ISOHYDRIC pH VALUE OF SOILS AND ITS DETERMINATION

Fig. 1. Isohydic Titration Curves of Soils.....	52
2. The pH Values of Soils as Determined by Different Workers and by Different Methods .....	54

## MICROBIAL ACTIVITIES IN SOIL: IV. MICROFLORA OF DIFFERENT ZONAL SOIL TYPES DEVELOPED UNDER SIMILAR CLIMATIC CONDITIONS

Fig. 1. Numbers of Bacteria, Actinomycetes, and Fungi per Gram of Dry Soil in Palouse Silt Loam (Pullman).....	60
2. Numbers of Bacteria, Actinomycetes, and Fungi per Gram of Dry Soil in Palouse Silt Loam (Troy).....	61
3. Numbers of Bacteria, Actinomycetes, and Fungi per Gram of Dry Soil in Helmer Silt Loam.....	62
4. Percentages of Soil Moisture Based on Dry Weight at Different Depths and Sampling Periods .....	64

## THE MOVEMENT OF WATER IN HEAVY SOILS AFTER IRRIGATION

Fig. 1. Moisture Profiles Illustrating Effect of Different Surface Conditions on the Calculated Profiles for Eastern Gezira Soil.....	98
2. Comparison Between Observed and Calculated Moisture Profiles for Gezira Soil to Which 1 Ton of Gypsum per Acre Had Been Applied .....	99
3. Moisture Profiles for Gezira Soil to Which 4 Tons of Gypsum per Acre Had Been Applied .....	100
4. Comparison Between Observed and Calculated Moisture Profiles for Gezira Soil to Which 10 Tons of Gypsum per Acre Had Been Applied. ....	101
5. Comparison Between Observed and Calculated Moisture Profiles at Various Intervals After Irrigation. ....	102

## HYDROGEN-ION ACTIVITY OF COLLOIDAL ACIDS IN SOILS

Fig. 1. Relation Between pH Value and Hydrolysis of Ethyl Acetate.....	114
2. Effect of Temperature on Hydrolysis of Ethyl Acetate by Soil and KCl-HCl Buffer at pH 2.03 .....	117
3. Effect of Time of Shaking and of Quantity of Soil on the Hydrolysis of Ethyl Acetate .....	118
4. Effect of Concentration of Ethyl Acetate on Hydrolysis by Soil.....	119
5. Relation between pH Values and Sugar Inversion. Na-Acetate-Acetic Acid Buffer, 4 Hours' Shaking at 60°C.....	124
6. Effect of Temperature on Inversion by P.C. 13 Soil.....	125
7. Relation between Quantity of Soil and Inversion of Sugar.....	126

## MICROBIAL ACTIVITIES IN SOIL: V. MICROBIAL ACTIVITY AND ORGANIC MATTER TRANSFORMATION IN PALOUSE AND HELMER SOILS

Fig. 1. Carbon Dioxide Production and Number of Microbes in Variously Treated Helmer Silt Loam.....	143
2. Carbon Dioxide Production and Number of Microbes in Variously Treated Palouse Silt Loam.....	144
3. Bacteria in Helmer Silt Loam and in Palouse Silt Loam .....	146
4. Actinomycetes in Helmer Silt Loam and in Palouse Silt Loam.....	147
5. Fungi in Helmer Silt Loam and in Palouse Silt Loam.....	149
6. Aerobic Cellulose-Decomposing Bacteria in Helmer Silt Loam and in Palouse Silt Loam.....	150
7. Organic Carbon Fractions in Percentages of the Amounts Present in the Soil at the Beginning of the Experiment.....	154



8. Nitrogen Fractions in Percentages of the Amounts Present in the Soil at the Beginning of the Experiment ..... 154
9. Eh and pH Values of Helmer and Palouse Silt Loams ..... 158

#### CATION EQUILIBRIA IN PLANTS IN RELATION TO THE SOIL

- Fig. 1. Relation Between Exchangeable Calcium in the Soil and Its Concentration in the Plant ..... 179
2. Relation Between Exchangeable Magnesium in the Soil and Its Concentration in the Plant ..... 179
  3. Relation Between Exchangeable Sodium and Potassium in the Soil and Their Concentrations in the Plant ..... 180
  4. Relation Between the Soil Value for Exchangeable Calcium, Calculated by the Given Formula, and the Concentration in the Plant ..... 183
  5. Relation Between the Soil Value for Exchangeable Magnesium, Calculated by the Given Formula, and the Concentration in the Plant ..... 184
  6. Relation Between the Soil Value for Exchangeable Sodium, Calculated by the Given Formula, and the Concentration in the Plant ..... 184
  7. Relation Between the Soil Value for Exchangeable Potassium, Calculated by the Given Formula, and the Concentration in the Plant ..... 185

#### AN EVALUATION OF THE NEUBAUER AND THE CUNNINGHAMELLA AND ASPERGILLUS NIGER METHODS FOR THE DETERMINATION OF THE FERTILIZER NEEDS OF A SOIL

- Fig. 1.  $P_2O_5$  Content of Limed and Unlimed Plot Sections of Cumberland Loam at the Knoxville Station, as Determined by the Neubauer and the Cunninghamella Methods ..... 221
2.  $K_2O$  Content of Limed and Unlimed Plot Sections of Cumberland Loam at the Knoxville Station, as Determined by the Neubauer and the *Aspergillus niger* Methods ..... 222

#### BEHAVIOR OF CALCIUM, MAGNESIUM, AND POTASSIUM SULFATES, AS INFLUENCED BY LIMESTONE AND BY DOLOMITE—A LYSIMETER STUDY

- Fig. 1. Outgo of Calcium, Magnesium, and Potassium from a Sod-Skimmed Soil Treated with Seven Annual Equivalent Incorporations of Sulfates of Calcium, Magnesium, and Potassium, with and without a Single Initial Addition of Either Limestone or Dolomite ..... 240

#### INFLUENCE OF SALTS AND SOIL-WATER RATIO ON pH VALUE OF SOILS

- Fig. 1. Effect of Magnesium, Lithium, Strontium, and Barium Chlorides on the pH Values of their Corresponding Soils ..... 253

#### EFFECT OF "ALKALI" SALTS ON GENERAL MICROBIAL FUNCTION IN SOIL

- Fig. 1. Effect of "Alkali" Salts on Organic Decomposition in Willamette Silty Clay Loam ..... 290
2. Effect of Treatment on Carbon Dioxide Evolved from Virgin Saline Soil ..... 296
  3. Effect of Treatment of Carbon Dioxide Evolved from Reclaimed Saline Soil ... 296

#### FURTHER STUDIES OF BACTERIUM GLOBIFORME AND THE INCIDENCE OF THIS TYPE OF ORGANISM IN CANADIAN SOILS

- Fig. 1. Correlation of Characters of *Bact. globiforme*, Types I and II ..... 317

## OXIDATION-REDUCTION POTENTIALS IN SOILS

Fig. 1. Relation between pH and $E_h$ of Single-Base Soils.....	325
2. Relation between pH and $E_h$ of Various Colloidal Substances.....	327
3. Stabilization of pH- $E_h$ Relationship by Clay and Artificial Zeolite in Buffer Solution.....	328

## THE CHEMICAL COMPOSITION OF SOIL FROM CULTIVATED LAND AND FROM LAND ABANDONED TO GRASS AND WEEDS

Fig. 1. Nitrogen in Cultivated and Uncultivated Soils at Different Periods.....	382
2. Carbon in Cultivated and Uncultivated Soils at Different Periods.....	382

## INTERACTION BETWEEN CARBONATES AND SOILS

Fig. 1. Titration of Sodium Carbonate with Various Acids and with Soil Acidoid.....	402
2. Titration of Sodium Carbonate with Calcium Salts and with Calcium Soil.....	403
3. Titration of Calcium Carbonate with Various Acids and with Soil Acidoid.....	405
4. Influence of Calcium and Sodium Salts and of Corresponding Soils on the pH Value of Calcium Carbonate Suspension.....	407
5. Titration Curve of H-Soil with Calcium Carbonate.....	408

## ORGANIC PHOSPHATES: I. FIXATION STUDIES WITH THREE DIFFERENT SOIL TYPES

Fig. 1. Time Dependence Curves of Immobilization of Organic and Inorganic Phosphates by Raw and Sterilized Norfolk Soil.....	413
2. Time Dependence Curves of Immobilization of Organic and Inorganic Phosphates by Raw and Sterilized Las Vegas Soil.....	413

## OBSERVATIONS REGARDING SOILS OF NORTHERN AND CENTRAL MEXICO

Fig. 1. Rainfall Map of a Part of Mexico.....	429
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## RESULTS OF LYSIMETER EXPERIMENTS

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*Soil Laboratory, Versailles, France*

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Experiment stations in different countries have been using lysimeters for many years. These lysimeters differ from one another according to the contemplated research work. In many places it was deemed necessary to leave the soil *in situ* with its profile structure undisturbed; such a condition is indispensable for obtaining results which measure what really takes place in the field. Consequently the gauges may reach a depth of 2 m.

In our own researches we have used lysimeters to study a few processes related to pedogenesis under natural conditions. The tanks are waterproof cement boxes, 1 m. square and 0.6 m. deep. The dimensions of the boxes efficiently minimize the influence of the walls, and the square shape is favorable for seedlings. Three of the sides are in contact with the soil, the fourth is isolated by a layer of cork 6 cm. thick; samples can be taken at different depths through holes conveniently spaced.

### EXPERIMENTS WITH LOAM

Each tank used in the loam experiments was filled in 1929 with 720 kgm<sup>•</sup> of an air-dried homogeneous soil consisting of the arable layer of a loam and having the composition shown in table 1. The tanks were left undisturbed for 2 years before observations were made. In 1931 we ascertained that all the tanks had become uniform and that the experimental error in the comparisons would be small enough to justify the conclusions drawn from the different treatments.

Drainage waters have been analyzed monthly, for the purpose of studying the balance of water and of the main mineral elements. Some lysimeters have been kept free from vegetation; others were cropped annually as follows: 1932, barley; 1933, carrots; 1934, wheat; 1935, oats; 1936, maize. Some of the tanks received special treatments, in duplicate, as follows: mulching (with paper), addition of organic matter (500 gm. straw per square meter in October), irrigation by porous pipes.

### *Loss of water*

As a rule, no water drains through the tanks during summer, but water flows again at times during winter. Whether cropped or uncropped, tanks always showed the same drainage of water by the end of winter; therefore, each annual cycle was started March 1.

Under the climatic conditions of the region around Paris, drainage water results mostly from winter rains, which occur when nitrification is almost stopped and the biological activity of the soil is very low. In our tanks (the retention capacity of which is about 140 mm. of rainfall) a notable quantity of nitrates may escape leaching in dry years such as 1933 and be carried over to the next year.

On the other hand, the quantity of nonleached nitrates is lower than 10 kgm. per hectare and therefore not to be taken into account in years that average more than 200 mm. of rainfall during winter. Checking over the

TABLE 1  
*Composition of the loam in lysimeters at Versailles*  
(Parts per thousand air-dried soil)

PHYSICAL ANALYSIS		CHEMICAL ANALYSIS	
Coarse sand .....	20	CaO exchangeable .....	3.95
Fine sand .....	655	CaO carbonates .....	1.10
Silt .....	132	MgO exchangeable .....	0.25
Clay .....	136	K <sub>2</sub> O exchangeable .....	0.09
Calcareous .....	2	N total .....	1.80
Organic matter .....	28	P <sub>2</sub> O <sub>5</sub> available .....	0.15
Humus .....	11	C total .....	10.40

TABLE 2  
*Effect of cropping on evaporation and drainage of rainfall from lysimeters*

	1932		1933		1934		1935		1936		AVERAGE	
	Uncropped	Cropped	Uncropped	Cropped	Uncropped	Cropped	Uncropped	Cropped	Uncropped	Cropped	Uncropped	Cropped
Rainfall, mm. . . . .	505.4	505.4	398.9	398.9	665.9	665.9	732.4	732.4	656.4	656.4	591.8	591.8
Drainage, per cent. . . . .	39.6	23.7	27.4	15.2	39.2	33.5	42.7	34.8	46.7	35.1	40.2	30.0
Evaporation, per cent. . . . .	60.4	76.3	72.6	84.8	60.8	66.5	57.3	65.2	53.3	64.9	59.8	70.0

results of a series of properly selected years made possible the tabulation of the data into a closed cycle, in such a way that the state at the end of the experiment duplicated that at the beginning. From such a closed cycle reliable information as to the translocation of soluble salts could be obtained.

The difficulty of obtaining experimental results on evaporation that are representative of the phenomena taking place in the field is well known. In the lysimeter the deep layers of the soil are eliminated, but in many investigations under wet climatic conditions the influence of these layers is of little importance. Table 2 gives our observations for the last 5 years, which may be regarded as including the extremes for northern France.

The annual evaporation from uncultivated land averages 59.8 per cent, ranging from 53.3 to 72.6 per cent. Cropped land evaporated, on the average, approximately 17 per cent more water (corresponding to 60 mm.) than did fallow land. It is evident that this supplementary loss is much smaller than the loss due to transpiration. This fact corroborates our knowledge of the "shading effect" of vegetation, which reduces evaporation from the soil itself.

### *Loss of mineral constituents*

Table 3 shows the average annual loss of the principal minerals and nitrogen for 5 successive years.

Except for P and K (the loss of which is almost entirely accounted for by the crops), it has been noted that crops have always lowered the losses of minerals from the soil; this is particularly true for CaO. Under the climatic conditions of northern France, loss of calcium is intensified in fallow soils, because leaching is increased. Fertilization can modify this. The annual

TABLE 3  
*Average annual loss of mineral constituents*  
(Kilograms per hectare)

	UNCROPPED	CROPPED			B - A
	Drainage (A)	Drainage	Crops	Total (B)	
CaO . . . . .	553.6	357.8	23.9	381.7	-171.9
MgO . . . . .	48.4	31.5	10.7	42.2	-6.2
K <sub>2</sub> O . . . . .	12.7	6.9	79.0	85.9	+73.2
N. . . . .	168.2	82.1	59.3	141.4	-26.8
S. . . . .	86.7	71.9	10.0	81.9	-4.8
P <sub>2</sub> O <sub>5</sub> . . . . .	0.35	0.22	31.5	31.72	+31.3

addition to the lysimeters of 12.5 kgm. of artificial manure per square meter increased the loss of CaO through drainage by 23 per cent (132 kgm. CaO per hectare).

In tanks where the soil was uncropped, the ratio MgO/CaO in drainage water was more or less constant (1/8), the ratio between exchangeable Mg and exchangeable Ca in soil being 1/12. In tanks with crops this ratio increased because plants contain more magnesium than calcium.

### *Loss of nitrogen*

In fallow soils 1.30 per cent of the nitrogen reserve in the soil (1.80 parts per thousand) is nitrified each year on the average, which amounts to 84 kgm. per hectare for a 0.3-m. layer, variations depending on the climatic characteristics of any particular year. Cropping decreased the nitrogen loss (crops + drainage) by 16 per cent. This fact has already been observed by Deherain (1), by Warrington (8), by Russell (6), and by Lyon (3). The decrease may be due to a decrease in the formation of nitrates or to an increase

in the utilization of nitrates formed. The second hypothesis is favored by the following observations:

The effect of cropping on nitrogen removal was observed in tanks which were provided with subterranean irrigation in dry seasons or which had been mulched. The decrease of nitrates is not correlated, therefore, with an inhibition of nitrification by the drying of the soil as a consequence of cropping.

If nitrogen reserves were really spared in the cropped tanks, these lysimeters, in the course of time, should reach a higher level of nitrified nitrogen than the uncropped ones, a situation which has not been observed as yet.

From data in table 3 we see that the diminution of the calcium salts removed by the tanks without crops (171.9 kgm. CaO) corresponds to the difference in the removal of nitrates by drainage [168.2 - 82.1 = 86.1 kgm. N, corresponding to 172 kgm. CaO as  $\text{Ca}(\text{NO}_3)_2$ ], which favors the conclusion that the biological activity has been the same in both cases.

Nitrate accumulation decreased only during the first year in the lysimeters that received straw; the added organic matter slowly but progressively nitrifying as shown in table 4.

In short, we believe that cropping results in the consumption of a certain quantity of nitrates in addition to the quantity used up for the nutrition of the plants, as a result of an increased activity of microbes on the soil, which

TABLE 4  
*Influence of straw on nitrate formation in an uncropped soil*

TREATMENT	1933	1934	1935	1936
No straw . . . . .	100	100	100	100
Straw added, 500 gm. per square meter annually	93.3	99.6	107	114.6

may be due to easily decomposable non-nitrogenous organic matter. This view is supported by the fact that in pot cultures the coefficient of nitrate utilization is always less than 100 per cent.

#### WEATHERING OF GRANITE

In lysimeter experiments on the weathering of granite, each tank was filled with 800 kgm. of granite rock<sup>1</sup> that had previously been crushed and sifted into pieces ranging from 2 to 4 mm. in diameter. The drainage water, which was always clear, was periodically collected, measured, and analyzed. The change in the granite was observed after 5 years' exposure to natural conditions without vegetation.

#### *Mechanical analysis of weathered granite*

Mineral colloids were extracted, without acid pretreatment, by the following dispersion method, which induces the least alteration (5):

Destruction of organic matter by hydrogen peroxide.

Washing with 0.1 N KCl to eliminate the soluble Ca salts.

Peptization in the presence of  $\text{Na}_2\text{CO}_3$  (concentration 5 m.e. per liter).

<sup>1</sup> Composed of quartz, orthoclase, muscovite, and biotite.

The separation of the fine particles was then made as usually by settling and decantation.

The whole mass contained approximatively equal amounts of the three fractions, 1-2 mm., 0.2-1 mm., and less than 0.2 mm. Particles representing the clay fraction ( $< 2 \mu$ ) amount to 0.8 per cent, uniformly distributed from top to bottom of the lysimeter (2). The disintegration of granite, therefore, proceeded evenly in the whole mass, without expenditure of mechanical energy for the translocation of materials, and solely as a result of climatic factors (rain, temperature). No migration of the smallest particles occurred. It has been noted, moreover, that below  $200\mu$  the separation of the mineral species was more or less complete.

TABLE 5

*Chemical analyses of original granite, of weathered granite, and of two natural clays*

	ORIGINAL GRANITE.	WEATHERED GRANITE			GRANITIC SOIL B HORI- ZON	BRICK EARTH B HORI- ZON
		Silt 20 - 2μ	Clay			
			2 - 0.75μ	<0.75μ		
SiO <sub>2</sub> ..... per cent	74.75	69.43	60.72	55.61	42.40	48.90
Al <sub>2</sub> O <sub>3</sub> ..... per cent	13.50	15.95	21.59	22.98	31.05	25.40
Fe <sub>2</sub> O <sub>3</sub> ..... per cent	1.50	2.22	2.70	2.82	7.85	8.70
TiO <sub>2</sub> ..... per cent	.	.	.	0.50	0.64	0.86
CaO..... per cent	0.93	0.98	0.99	1.12	0.30	0.22
MgO..... per cent	0.59	0.93	1.46	2.03	0.51	1.26
K <sub>2</sub> O..... per cent	4.63	4.65	4.50	4.63	3.21	2.70
H <sub>2</sub> O..... per cent	0.90	2.10	4.06	7.54	10.95	9.77
Total..... per cent	.	.	96.02	96.73	96.27	96.95
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> .....	8.78	6.64	4.40	3.87	2.00	2.67
Base-exchange capacity..... m e.	.	.	61.00	67.00	81.00	82.00

#### *Chemical analysis of different fractions*

Organic matter must be thoroughly destroyed before chemical analyses are made, otherwise the results of studies on colloids are meaningless. Results of the chemical analyses of the original granite and of the different fractions of the weathered granite are given in table 5.

The analyses of different fractions show that chemical changes occur only in particles less than  $200\mu$ . As the size of particles diminishes, the relative importance of SiO<sub>2</sub> decreases and that of sesquioxides and water of hydration continuously increases. As far as the bases are concerned, the percentages of CaO and K<sub>2</sub>O are very low, but MgO increases markedly as the size of particles decreases. We must, therefore, conclude that biotite, more or more or less chlorinated, accumulates within the clay.

Comparison of the weathered granite with the original granite does not show the exact changes in the various elements; granite compounds (quartz, feldspar, mica) contribute unequally to the formation of colloidal fractions.



On the other hand, analysis of drainage water shows the importance of losses through leaching.

#### *Analysis of leachates*

During the 5 years under consideration, the rainfall totaled 2.806 mm., of which approximately 40 per cent, or 1.159 mm., was recovered as drainage water. Table 6 shows the mineral losses due to leaching.

Considering that 6.48 kgm. of clay was being formed and taking into account the elements which were adsorbed by these colloids, we can assume that  $\text{SiO}_2$  and  $\text{K}_2\text{O}$  released from the rock represent only a very small part of the quantity corresponding to a theoretical formation of clay:



The relative order of leaching out of basic material is as follows:  $\text{CaO} > \text{K}_2\text{O} > \text{MgO}$ , but  $\text{MgO}$  comes before  $\text{K}_2\text{O}$  if we consider the percentage of the whole quantity existing. The mass was not acidified below pH 6.85.

TABLE 6

*Losses of mineral substances in 1 square meter lysimeter containing 800 kgm. granite during a 5-year period (1931-1935)*

	TOTAL	PER CENT
	gm.	
Dry matter.....	387.3	...
After ignition .....	306.5	..
CaO.....	89.0	1.19
MgO.....	18.4	0.39
K <sub>2</sub> O.....	31.0	0.08
SiO <sub>2</sub> .....	19.7	0.003
S of sulfates.....	24.0	4.85
N of nitrates.....	4.8	4.85

The bases are leached out principally in the form of nitrates and sulfates. Silico-gel plates have shown that nitrifying organism rapidly colonize the mass. Moreover, it has been noted that the quantity of nitrogen as determined by analysis is almost equal to that which might have been contributed by rainfall during the 5-year period. Most of the sulfates result from the oxidation of sulfur present in the original granite (0.62 parts per thousand).

The fact that the ratio  $\text{SiO}_2/\text{K}_2\text{O}$  is close to 1 may signify that silica and potassium are washed out in the form of potassium silicate.

Finally, we can conclude that dissolution and hydrolysis, generally considered as fundamental processes, have contributed very little to the production of clay colloids. In this initial phase of weathering the phenomenon of hydration must be considered as prominent.

#### *Examination of clay colloids*

The two fractions  $2-0.75\mu$  and  $<0.75\mu$  were studied separately, and the colloids in these fractions were compared with those extracted from the B

horizon of two soils, one formed from the same parent rock and the other from a brick earth. The results are shown in table 5.

A comparison of the composition of these samples gives a measure of the extent to which chemical weathering has proceeded. In the newly formed clay, weathering increases gradually as the particles become finer. Moreover, we must note that the percentage of  $\text{SiO}_2$ , the ratio  $\text{SiO}_2/\text{R}_2\text{O}_3$ , and the percentages of nonexchangeable bases ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ) are higher in this immature clay than are those in the older soils. Titania has a tendency to accumulate with iron in the clay fraction. These considerations suggest an analogy between our juvenile clay and clays from glacial loams studied by O. Tamm.

From a physicochemical point of view, our juvenile clay displays every property common to clay colloids. Particularly, it behaves as a hydrophilic suspensoid and is sensitive to coagulating agents. The fixation capacity of bases is very similar to that of older clays, chiefly of the finest fraction.

This experiment gives us a view of the first stage of clay genesis in the weathering of granite under our climatic conditions. It shows that in a roughly comminuted mass, clay colloids are formed very early by a hydration process which preserves an important part of the combined bases. On this point, our observations agree with the conclusion of Zemiatchensky (9) concerning the transformation of feldspar in hydro-micas.

It should be added that we know of the existence of clays in which the phenomena of chemical alterations are weak (7, 9). We must, therefore, consider that Mattson's (4, 5) theory of clay formation by way of mutual precipitations of different colloids is correlated with secondary processes which take place in a more advanced stage.

These observations are also in agreement with the conception that the clay micelle is heterogeneous and is composed of a silicate core surrounded by a colloidal coating. It is easy to understand, thus, that clay can have a crystalline character, that it varies in its chemical composition, and that it is capable of evolution in soils under the influence of weathering.

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# THE LEACHING ACTION OF RAIN WATER UPON DOLOMITE AND LIMESTONE SEPARATES INCORPORATED WITH QUARTZ IN OUTDOOR LYSIMETERS

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Dolomite is used most extensively in the Coastal Plain, where many soils are made up of preponderant proportions of quartz and relatively small quantities of acidoids. Since many soils of such character have limited capacity to decompose added dolomite and to fix the calcium and the magnesium supplied thereby, direct solvent action upon the added raw dolomite may then supply nutritive calcium and magnesium.

A study was therefore made of the composition of rainwater percolations from chemically equivalent separates of limestone and of dolomite, incorporated in quartz. In such systems the factor of the behavior of the complexes formed by fixation of added calcium and magnesium is eliminated, and the influence of soil flora is at a minimal and near-constant level. The solvent action of rapid percolations in the readily permeated quartz medium would be expected to be less than the dissolving action of the more slowly moving percolates from sandy soils in which normal biological activities occur. The amounts of calcium and of magnesium removed from the quartz systems by rainwaters should be indicative, however, of the presumably more extensive solvent action within soil systems of high quartz content.

## MATERIALS AND TREATMENTS

All values used in the designation of rates of treatment and of quantities of calcium and of magnesium leached are in terms of calcium carbonate. Washed 20-40-mesh and 60-100-mesh separates of limestone and of dolomite were used in lysimeters having a surface area of 1/20,000 acre. The analyses of the limestone and of the dolomite separates are given in table 1. The two limestone separates had a common  $\text{CaCO}_3$ -equivalent value of 99.76 per cent and contained 0.94 per cent of  $\text{MgCO}_3$ . The dolomitic limestone contained calcium and magnesium carbonates in the approximate ratio of 51 to 38. The  $\text{CaCO}_3$ -equivalence of the 60-100-mesh dolomite separate was 96.7 and that of the 20-40-mesh separate was 94.5.

The limestone and the dolomite incorporations were made at the rates of 2, 13.3, and 53.1 tons per 2,000,000 pounds of quartz. Each treatment was incorporated only in the upper half of its quartz medium, although all percola-

tions were from the full depth of quartz. Within the zone of contact between quartz and incorporations, the several rates of treatment were therefore twice those respectively stipulated for the 100-pound charges of quartz. The upper zone of treatment and the lower untreated zone were separated by means of galvanized iron, asphaltum-coated, wire-cloth discs. The two larger incorporations were respectively equivalent to rates of 8 tons and 32 tons of CaO, these two rates having been used for additions of seven liming materials in a related earlier lysimeter study of a heavy type of soil.

The mixtures were placed in the 1/20,000-acre tanks June 20, 1931. The leachings from successive annual rainfalls of 44.12, 56.40, 49.61, and 55.34 inches were collected for the following 4-year period and analyzed for calcium, magnesium, dissolved carbonates, and sulfates. Quartz controls were placed

TABLE 1

*Analysis of separates of limestone and of dolomite incorporated in the quartz medium of the outdoor lysimeters*

	LIMESTONE*	DOLOMITE†	
		20-40 mesh	60-100 mesh
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Insoluble matter . . . . .	0.25	11.26	9.14
F <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> . . . . .	0.23	0.80	0.80
Ca, as CaCO <sub>3</sub> . . . . .	98.64	49.71	51.83
Mg, as MgCO <sub>3</sub> . . . . .	0.94	37.63	37.72
Total analyzed . . . . .	100.06	99.40	99.49
Mg, as CaCO <sub>3</sub> -equivalent . . . . .	1.12	44.80	44.90
Ca + Mg, as CaCO <sub>3</sub> -equivalent . . . . .	99.76	94.51	96.73

\* Purity of limestone assured uniformity in composition of different separates.

† A kiln-dried product containing small quantities of coal dust.

at each end of the row of lysimeters to collect rainwaters, so that the respective increments from quartz only could be determined.

#### LEACHATE VOLUMES

The individual leachates for the annual periods and for the 4-year period are given in table 2. Frequency of rainwater collections was governed by the periodicity of each annual rainfall. From June to June, there were 8 collections in 1931-32, 7 in 1932-33, 6 in 1933-34, and 6 in 1934-35.

The mean of the volumes that passed through the quartz controls was practically identical with the mean of the volumes that passed through the units that contained the minimal additions of limestone and of dolomite. Likewise, the 13-ton additions caused no appreciable difference in the amounts of water leached from the constant amount of quartz. There was, however, a definite diminution in the leachate volumes from the four treatments at the 53-ton

rate. This was noted in each of the 16 comparisons and is attributed to increased bulk rather than to physical change in the quartz in contact with the much larger incorporations of the two limestones.

TABLE 2  
*Leachates from limestone and dolomite in quartz media*  
Leachates expressed in kiloliters

LIMESTONE INCORPORATIONS			LEACHATES				
Type	Mesh*	Ton rate†	1931-32	1932-33	1933-34	1934-35	4-year average
Calcic	20-40	2	217	259	223	241	235
	"	13.3	215	256	223	241	234
	"	53.1	213	253	218	236	230
	60-100	2	215	259	225	242	233
	"	13.3	212	252	218	239	231
	"	53.1	204	236	203	223	217
Dolomitic	20-40	2	213	253	220	237	231
	"	13.3	212	251	221	238	231
	"	53.1	210	247	217	235	227
	60-100	2	211	250	221	239	230
	"	13.3	211	248	215	233	227
	"	53.1	202	233	198	221	214
Sand blank, north end‡		0	218	255	237	243	238
Sand blank, south end		0	214	252	219	237	231

\* Separates were washed before incorporation.

† Tons per 2,000,000 pounds of quartz.

‡ For collection of rainwater at each end of the row of lysimeters.

#### COMPOSITION OF LEACHATES

##### *Calcium content*

The data of table 3 represent the  $\text{CaCO}_3$ -equivalence of the calcium brought by rainwaters, supplemented by that dissolved in the upper zone and carried therefrom through the underlying zone of untreated quartz. The calcium content of rainwaters collected at a given point has been found to vary appreciably with season (7) and with the location of the tanks within a relatively small radius. The calcium content of rainwaters collected within a city will exceed that of collections made in adjacent rural sections. Waters collected in gauges and in blank lysimeters nearer the roadway invariably have a calcium content greater than that found in collections obtained in the more distant receptacles. A mean annual calcium increment of 161 pounds passed through the quartz controls at the north end of the installation, as against 136 pounds

for the more remote controls at the south end. The mean value of 149 pounds was used in correcting the total calcium outgo to determine the amounts actually derived from the limestone and the dolomite.

Magnitude of treatment was reflected in each of the 16 comparisons of annual outgo of calcium from both types of limestone, but the relationship between rate of addition and amounts leached was not proportionate. The total amounts of calcium derived solely from the 13-ton and 53-ton high-calcic

TABLE 3

*Calcium outgo in outdoor lysimeter leachings from limestone and dolomite incorporated in quartz medium*

Outgo expressed in pounds of  $\text{CaCO}_3$ -equivalence per 2,000,000 pounds of quartz medium

LIMESTONE INCORPORATIONS WITH QUARTZ			OUTGO						
Type	Mesh*	Ton rate†	1931-32	1932-33	1933-34	1934-35	Total	Mean Annual	
								Actual	Cor- rected for blanks
Calcic	20-40	2	233.6	266.8	239.5	250.2	990	248	99
	"	13.3	294.4	361.3	295.4	337.6	1,288	322	173
	"	53.1	371.6	435.0	341.4	398.2	1,546	387	238
	60-100	2	212.2	281.6	226.7	246.1	967	242	93
	"	13.3	355.3	404.1	329.9	371.2	1,461	365	216
	"	53.1	433.4	465.4	354.3	443.0	1,696	424	275
Dolomitic	20-40	2	165.2	188.4	195.9	199.9	749	187	38
	"	13.3	223.2	255.6	238.1	242.5	959	240	91
	"	53.1	293.6	320.4	257.5	285.6	1,157	289	140
	60-100	2	176.8	184.9	184.2	180.1	726	187	33
	"	13.3	302.6	307.5	250.3	265.0	1,125	281	132
	"	53.1	386.9	386.6	313.6	364.1	1,451	363	214
Quartz blank, north end‡		0	156.4	162.0	176.8	148.6	644	161	.
Quartz blank, south end		0	129.0	121.2	153.5	140.2	544	136	...

\* Separates were washed before incorporation.

† Tons per 2,000,000 pounds of quartz.

‡ For collection of rainwater at each end of the row of lysimeters.

limestone treatments were only 2.1 times and 2.6 times the corrected total calcium outgo from the 2-ton treatment. The total amounts of calcium derived solely from the 13-ton and 53-ton dolomite treatments were 3.1 and 4.9 times the amount of calcium actually leached from the 2-ton dolomite addition.

Comparable amounts of calcium were leached from the 20-40-mesh and 60-100-mesh separates of limestone at the 2-ton rate. This was true also of

the less extensive amounts of calcium leached from the 2-ton incorporations of the two corresponding dolomite separates.

The 96-pound mean annual net loss of calcium from the 2-ton incorporations of the two limestone separates exceeded the 70-pound increase in annual outgo from a 3,570-pound  $\text{CaCO}_3$ -equivalent addition of 100-mesh limestone to the upper zone of a black Onslow sandy soil at the Virginia Station (3, p. 13). When incorporated to full depth in the same black soil, the 3,570-pound limestone treatment caused an increase of 124 pounds in the calcium outgo. The corresponding surface and full-depth 3,570-pound incorporations of dolomite in the black Virginia soil caused annual increases in calcium outgo of only 11 and 8 pounds, respectively. When additions beyond fixation-capacity are made, the undecomposed dolomite and the fixed calcium and magnesium produce divergent proportions of dissolved calcium and magnesium in the soil system (2).

The effect of fineness was definitely registered by the composition of the leachates from the two heavier additions. Every annual outgo of calcium from the 60-100-mesh limestone additions at the 13-ton and 53-ton rates, exceeded the corresponding annual outgo from the corresponding incorporation of the 20-40-mesh material. This was true also for the analogous comparisons for calcium outgo from the finer and coarser dolomite separates. In each of the six comparisons of calcium actually derived from the limestone and dolomite separates, the limestone separate yielded the larger quantity of calcium. The mean of the amounts of calcium derived from the six limestone separates was twice the mean of amounts actually leached from the six separates of dolomite.

#### *Magnesium content*

The quantities of magnesium leached from the separates of limestone and of dolomite are given in table 4. As would be expected, the meager magnesium carbonate content of the limestone did not yield an appreciable quantity of magnesium to the leachates. Moreover, the dominance of calcium carbonate caused an invariable diminution in the magnesium content of the rainwaters during their percolation through the limestone-quartz systems, the amount of magnesium leached from each of the six limestone additions being less than the magnesium content of the rainwaters. A similar phenomenon has also been noted as the characteristic effect produced upon the outgo of magnesium from native noncarbonate forms in soils that received *full-depth* incorporations of high-calcic liming materials (2, 3, 5, 6).

Each dolomite addition induced an increased outgo of magnesium, the increases being in the order of rate of addition. Magnesium outgo and rate of dolomite addition were, however, not proportionate. The mean net amounts of magnesium leached from the two 13-ton and the two 53-ton dolomite separates were, respectively, 2.5 and 4.1 times the net amount leached from the two 2-ton additions.



The influence of fineness of the dolomitic separates upon the amounts of magnesium leached was definite, although not extensive. The 60-100-mesh separate yielded more magnesium than did the 20-40-mesh material. This held for each of the three rates.

The differences between the outgo of the magnesium content of the raw dolomite and the outgo of the magnesium in the complex derived from added dolomite are apparent from a comparison of the leachates from the 2-ton addition of 60-100-mesh dolomite in the quartz medium and 3,570-pound  $\text{CaCO}_3$ -

TABLE 4

*Magnesium outgo in outdoor lysimeter leachings from limestone and dolomite incorporated in quartz medium*

Outgo expressed in pounds  $\text{CaCO}_3$ -equivalence per 2,000,000 pounds of quartz medium

LIMESTONE INCORPORATIONS WITH QUARTZ			OUTGO						Mean annual	
Type	Mesh*	Ton rate†	1931-32	1932-33	1933-34	1934-35	Total		Actual	Corrected for blanks
Calcic	20-40	2	28.7	44.5	24.5	23.3	121.0	30.3		-6.2
	"	13.3	28.5	33.9	19.6	20.2	102.2	25.6		-13.5
	"	53.1	22.6	25.7	21.1	18.7	98.1	24.5		-12.0
	60-100	2	28.4	45.6	19.8	23.4	117.2	29.3		-7.2
	"	13.3	28.9	37.7	21.1	20.0	107.7	26.9		-9.6
	"	53.1	30.5	37.4	21.5	20.7	110.1	27.5		-9.0
Dolomitic	20-40	2	36.6	68.0	34.9	51.3	190.8	47.7		11.2
	"	13.3	57.0	90.7	56.6	72.4	276.7	69.2		32.7
	"	53.1	85.2	101.4	70.8	79.7	337.1	84.3		47.8
	60-100	2	41.9	69.3	42.9	62.1	216.2	54.1		17.6
	"	13.3	69.8	94.1	59.7	77.0	300.6	75.2		38.7
	"	53.1	122.1	124.4	84.7	97.6	428.8	107.2		70.7
Quartz blank, north end‡		0	31.7	54.0	28.2	33.1	147.0	36.8		.....
Quartz blank, south end		0	29.2	50.0	30.9	34.5	144.6	36.2		.....

\* Separates were washed before incorporation.

† Tons per 2,000,000 pounds of quartz.

‡ For collection of rainwater at each end of the row of lysimeters.

equivalent incorporations of similar dolomite of 100-mesh fineness in the black sandy soil used in the Virginia Station studies (3, p. 21). A net loss of only 17.6 pounds was registered as an annual outgo from the dolomite-quartz systems, whereas corresponding annual net losses of 78 and 89 pounds were found for the surface-zone and full-depth incorporations of the 3,570-pound additions of dolomite to the fallow Virginia soil. This difference is also partly attributable to the presumably higher  $\text{H}_2\text{CO}_3$  concentrations that prevailed in the Virginia soil.

*Total calcium plus magnesium*

Table 5 shows the total quantities of Ca + Mg leached from the high-calcic limestone that contained only 0.94 per cent magnesium carbonate and from the dolomite that contained 52 per cent calcium carbonate and 38 per cent magnesium carbonate. The greater solubility of the high-calcic limestone was reflected by the fact that, for each of the three rates, the total Ca + Mg

TABLE 5

*Total Ca + Mg and carbonates leached by rainwater during a 4-year period from limestone and dolomite separates incorporated in quartz medium in outdoor lysimeters*

Outgo expressed in pounds CaCO<sub>3</sub>-equivalence per 2,000,000 pounds of soil

LIMESTONE INCORPORATIONS WITH QUARTZ			OUTGO OF Ca + Mg						
Type	Mesh*	Ton rate†	4-year period		Mean of annual				Proportion accounted for by carbonates
			Total	As carbonate	Actual	Net‡	As carbonate		
							Actual	Net‡	
Calcic	20-40	2.0	1,111	1,101	278	93	275	90	per cent
	"	13.3	1,390	1,377	348	163	344	159	97
	"	53.1	1,644	1,572	411	226	393	208	98
	60-100	2.0	1,084	1,094	271	86	274	89	92
	"	13.3	1,569	1,527	392	207	382	197	100+
	"	53.1	1,806	1,730	452	267	433	248	95
Dolomitic	20-40	2.0	940	956	235	50	239	54	93
	"	13.3	1,236	1,141	309	124	285	100	100+
	"	53.1	1,494	1,377	374	189	344	159	81
	60-100	2.0	942	942	236	51	236	51	84
	"	13.3	1,426	1,342	357	172	336	151	100
	"	53.1	1,880	1,666	470	285	417	232	88
Quartz blank, north end§		0	791	816	198	...	204	...	..
Quartz blank, south end		0	689	661	172	...	165	...	..

\* Separates and quartz washed before incorporation.

† Tons per 2,000,000 pounds of quartz.

‡ Amounts derived from limestone or from dolomite; difference between outgo from quartz-limestone, quartz-dolomite units and rainwater leachings through quartz blanks.

§ For collection of rainwater at each end of the row of lysimeters.

leached from each limestone separate exceeded the Ca + Mg outgo from the corresponding dolomite separate. The mean of the total amounts of Ca + Mg carried by the rainwaters that passed through the six limestone incorporations was 1,436 pounds for the 4-year period, as against 1,320 pounds for the six dolomite incorporations. The mean total amounts of Ca + Mg actually derived from the six incorporations of limestone and of dolomite during the

4-year period, however, were only 696 pounds and 580 pounds  $\text{CaCO}_3$ -equivalence, respectively, or mean annual losses of 174 pounds and 145 pounds. The net losses indicate that the limestone was 1.2 times as soluble as the dolomite. When the same limestone and the same dolomite were extracted by six successive daily digestions with carbonated water, the solubility of the high-calcic limestone was found to be 2.48 times that of the dolomite (1). The true relationship between the solubility of limestone and that of dolomite in the rainwater leachates is masked, however, by the effect of the calcite content of the dolomitic limestone. Previous studies have shown that this particular dolomitic limestone contains 8–10 per cent of calcite in the interstices between the crystals of true dolomite. It has been noted that the interstitial calcite is dissolved faster than the dolomite (4). When the earlier extractions are filtered from the suspended rock, they therefore contain more calcium than magnesium, but successive subsequent extractions of the less soluble dolomite fraction bring calcium and magnesium into solution at the constant ratio of 1:1 (4).

The limestone and the dolomite of the present study were also used in the Virginia Station studies, which afforded comparative data as to the 4-year outgo of  $\text{Ca} + \text{Mg}$  induced by an annual rainfall of 33.8 inches, (3, p. 25). A net outgo of only 123 pounds of  $\text{Ca} + \text{Mg}$  was induced by the full-depth incorporation of a 3,570-pound  $\text{CaCO}_3$ -equivalence of high-calcic limestone in Onslow fine sandy loam, as against 72 pounds from surface-zone incorporation of limestone. The corresponding full-depth incorporation of dolomite gave a net  $\text{Ca} + \text{Mg}$  outgo of 97 pounds, whereas the surface-zone incorporation of dolomite gave a net  $\text{Ca} + \text{Mg}$  outgo of only 89 pounds.

#### *Calcium:magnesium ratios*

It has been pointed out that the ratio of  $\text{Ca}:\text{Mg}$  in the carbonated water extracts of true dolomite, as well as that of dolomitic limestones, is different from the one that holds for the composition of the respective leachates from high-calcic and dolomitic incorporations, subsequent to their fixation in soils. Moreover, the  $\text{Ca} + \text{Mg}$  from many dolomite fixations will either equal or exceed the  $\text{Ca} + \text{Mg}$  outgo from equivalent fixations from limestone treatments (3, 5, 6). The ratios of  $\text{Ca}$  to  $\text{Mg}$  in the rainwaters and in the leachates from the several dolomite separates can be seen by comparisons of the data of tables 3 and 4.

The  $\text{Ca}:\text{Mg}$  ratio in the rainwater percolates was 4:1. This proportion of magnesium is less than that found for previous directly collected rainwaters (7). The  $\text{Ca}:\text{Mg}$  ratio reported in the joint study (3, p. 12–21) were 2.12:1 and 1.82:1, respectively, for the Virginia and Tennessee Stations.

The 4:1 ratio of the rainwater percolates was altered in each of the six collections of percolates from the dolomite separates. After deduction of the calcium content of the rainwater percolates, the mean annual outgo of  $\text{CaCO}_3$ -

equivalence from the six dolomite separates was 108 pounds. A similar deduction for magnesium showed the mean annual outgo of 36.5 pounds as the  $\text{CaCO}_3$ -equivalence of the magnesium derived from the dolomite separates. These two values give a Ca:Mg ratio of 2.96:1. The proportion of Ca in this ratio is accentuated by the high proportion of calcium in the rainwaters and in the leachates from the calcite content of the dolomitic limestone, when only a small fraction of total charge of the latter is dissolved. As a cumulative effect—one not within the limited scope of the dissolving action of the rainwater upon the incorporations of dolomite in the quartz—the calcite passes more rapidly than the true dolomite, after which the Ca:Mg ratio in the leachates becomes stable, 1:1 (4). This indicates that the proportion of calcium in the early leachings from additions of dolomite in very sandy soils will be greater than that in the subsequent leachings.

### *Carbonate proportions*

Differing from rainwaters collected directly in standard rain gauges and in control lysimeters (3, 7), the rainwater leachates that passed through the ground quartz controls contained carbonates substantially equivalent to their Ca + Mg contents. Moreover, more than 90 per cent of the net outgo of Ca + Mg from each of the six limestone incorporations was accounted for by dissolved carbonates. The net Ca + Mg outgo from the 2-ton incorporations of dolomite was attributable to carbonates, which also accounted for more than 80 per cent of the Ca + Mg outgo from each of the four heavier treatments.

It has been observed that the sulfate content of rainwaters may vary markedly within a restricted area in which variable quantities of sulfur gases and sulfates are expelled to the atmosphere, especially where soft coal is used. Previous studies (7) have shown that the sulfur contents of rainwaters collected in gauges adjacent to the lysimeters of the present experiment are due chiefly to sulfates of calcium and magnesium, with a minor quantity attributable to sulfate of potassium. The entire sulfate contents of the rainwaters from the quartz blanks were computed, however, to the  $\text{CaCO}_3$ -equivalent values given in table 6. Each annual sulfate outgo from the control near the road exceeded the corresponding outgo from the more distant control. The same relationship held for the amounts of calcium, magnesium, and carbonates, as shown, respectively, in tables 3, 4, and 5.

No unqualified explanation can be advanced for the lower proportions of carbonates in the leachates from the heavier treatments of dolomite. Greater reactivity between magnesian components and hydrated  $\text{SiO}_2$ , occurring as films upon the extensive quartz surface, may have been partly responsible for the lower proportions of carbonates found in the leachates from the two heavier dolomite treatments.

An exact balance between total outgo of Ca + Mg and those reactions accounted for jointly by sulfates and carbonates is difficult to obtain, because

of the inherent error encountered in titrations of dilute solutions of carbonates and the magnification of that error when analytical values are computed to terms of pounds per 2,000,000 pounds of the quartz medium. The error incident to the titration of dissolved carbonates is a plus value and one that is proportionately larger in the titrations of the smaller quantities of carbonates carried by the leachates from the minimal rate of 2 tons. The sulfate incidence is, however, as nearly constant as experimental conditions would admit, and the magnitude of the differences between the several values for calcium, magnesium, and  $\text{Ca} + \text{Mg}$ , demonstrate the influence of the three variables, particle size, rate of treatment, and differential solubilities of the two types of limestone.

TABLE 6

*Ca + Mg attributable to sulfates in the rainwater leachates from the quartz blanks*

Leachate contents expressed in pounds per 2,000,000 pounds of quartz

ANNUAL PERIOD*	DETERMINED SULFATE SULFUR			SULPHATES COMPUTED TO $\text{CaCO}_3$		
	North end†	South end‡	Mean	North end†	South end‡	Mean
1932	25	21	23.0	78	66	72
1933	22	18	20.0	69	56	63
1934	17	14	15.5	53	44	49
1935	22	19	20.5	69	59	64
4-year total...	86	72	79.0	269	225	248
Mean...	22	18	20.0	67	56	62

\* July to July.

† Quartz blank nearer to road.

‡ Quartz blank farther from road.

#### ADAPTATION OF FINDINGS

The results indicate the importance of a fine state of division and of judicious incorporations of limestone or of dolomite to assure adequate supplies of nutrient calcium and magnesium for soils of high quartz content. This holds especially for the less soluble dolomitic limestone. A conclusion seems warranted by a comparison of the composition of the leachates from the limestone-quartz and dolomite-quartz mixtures with the composition found for leachates obtained during the first 4 years after incorporations of limestone and of dolomite in a black Onslow fine sandy loam. The unfixed fractions of finely divided high-calcic limestone will give to the free soil-water a calcium concentration greater than that resultant from comparable quantities of calcium held in the soil complex, and a consequential decrease in the amounts of magnesium derived from the native magnesian components of the soil. Undecomposed incorporations of dolomite are less soluble than the fixation complexes that follow disintegration of the dolomite. After the dolomite undergoes disintegra-

tion in the soil, the amounts of magnesium dissolved from the magnesian complexes by the free soil-water may exceed the amounts of calcium dissolved from the calcic complexes. The quantities of magnesium derived from rainwaters, from soil, and from dolomite additions, and the aggregate supplies of calcium from the same sources are in such relationship that a toxic excess of magnesium will not occur. The desirability of maintaining an adequate supply of organic matter not only to develop a  $\text{CO}_2$ -impregnated soil-water to dissolve the incorporated limestones but also to produce organic complexes capable of fixing the calcium and magnesium supplied by the added limestones is also indicated.

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# AN EFFICIENT AND CONVENIENT TYPE OF COOLING AND FREEZING BATH

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The dilatometer method has proved to be an excellent means of determining the permanent wilting point of soils (2) and the moisture equivalent of soils (3). Investigations now under way reveal that it can be used also to determine the normal field moisture capacity of soils. In all of these determinations, the dilatometer with its contents must be cooled and maintained at a temperature of exactly  $-1.0^{\circ}\text{C}$ . The type of cooling bath that has been employed heretofore in these investigations, as well as in previous freezing point determinations, consisted of a small earthenware jar placed inside a larger one, the space between them being filled with asbestos fiber and sealed with melted paraffin (1). This type of cooling bath has never worked entirely satisfactorily, principally because the paraffin would either crack or draw away from the jar through contraction and thus allow water to enter the air space. When the air space became wet, the bath would not keep a constant temperature for any length of time. Furthermore, the earthenware jar, even though glazed, would absorb sufficient salt after long use to interfere in maintaining an exact temperature when the bath was freshly started.

Since the accuracy of the dilatometer method depends very largely upon maintaining an exact and constant temperature in the cooling bath, the necessity for a more efficient cooling bath is obvious. This necessity has led to the development of a new type of cooling bath (fig. 1) which has proved to be most efficient. It is made by placing a 12-quart galvanized steel pail inside a galvanized steel bushel basket, filling the space between them with rock wool, and sealing the top by brazing a strip of galvanized steel on the rims of the pail and the basket, thus making the insulating space permanently watertight and airtight. On the inside bottom of the pail is placed a piece of rubber-felt in order to provide a cushion for the dilatometer and thus minimize the danger of breakage. The inside of the pail is painted to prevent rusting. For a cover, a piece of rubber-felt is used, the felt side being waterproofed by paint.

The principal distinctive features of this new cooling bath may be summarized as follows:

It is permanent and nonbreakable, since it is made of metal.

Its insulating space is made permanently watertight and airtight, since it is sealed by brazing the joints.



It is extremely efficient; it will keep ice 3 or 4 days and a constant temperature with only occasional stirring.

It is light in weight, and the handles on the sides of the basket make it very convenient to handle and carry.

It is inexpensive and easily made.

This type of cooling bath may be used not only in connection with the dilatometer method but also in freezing point determinations generally.

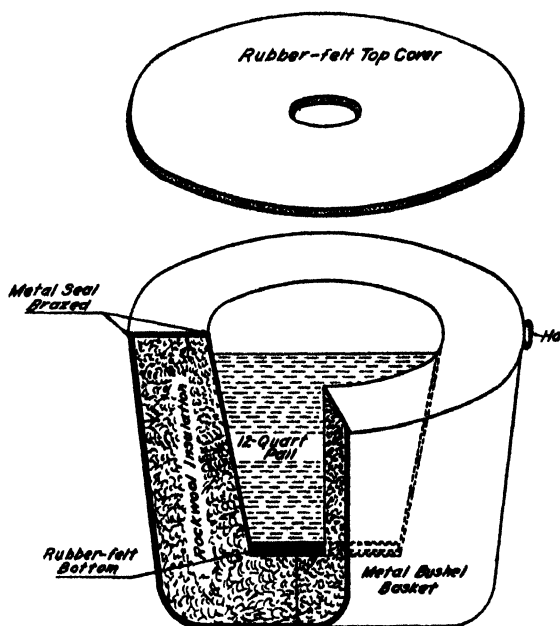


FIG. 1. AN EFFICIENT COOLING BATH USED IN CONNECTION WITH THE DILATOMETER METHOD AND IN FREEZING-POINT DETERMINATIONS

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## THE LATERITES OF WESTERN SAMOA

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The object of this paper is to discuss the soil process involved in the formation of immature laterite in the tropics and the practical problem of the recognition of the stage to which the lateritic process has proceeded—in other words to select characters of the soil that can be utilized for the mapping of series.

Western Samoa—including Upolu and Savaii—lying almost wholly between latitudes 13 and 14°S., has an equable, humid, tropical climate. The mean temperature at the coast in January is 79°F., and that in July, 77°F.; progressively lower temperatures are, of course, experienced inland. The rainfall is 111 inches at Apia on the coast of Upolu; 200 inches at Tiavi (2,450 feet), the highest point at which observations were made in Upolu; and 170 inches 4 miles inland from Tuasivi on Savaii.

Basalt is almost everywhere the parent material of the soil; on the coast there is, in most places, a low-lying border a few chains wide in which an admixture of coral sand occurs. Observations were confined to the soils derived from the lava flows on the gentle slopes on the north of Upolu and on the east of Savaii. The flows are not all weathered to the same extent; where differences occur in the same climatic area, the flows are obviously not of the same age. In most localities the subsoil extends from 5 to 6 feet below the surface. Probably the basalts range in age from Pleistocene to Recent. Analysis (table 1) shows the composition of the fresh rock, which agrees fairly closely with that of ordinary basalts, except that titania is well above the usual amount.

Rain forest is the natural vegetation, and where this is cleared a thick mat of weeds soon develops unless weeding is practised. On the forest floor is a shallow leaf litter, less than an inch thick. The commercial crops grown in the areas examined are coconuts, cocoa, and bananas. Virtually no manuring has been done to date.

### DESCRIPTION OF SOILS

The following soil types have been recognized: Saleimoa stony sandy loam, Vaitele stony clay loam, Magia stony clay loam, Tuasivi clay loam, Malatula

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stony clay loam, and Tiavi clay loam. These are arranged according to the degree of leaching which they are thought to have undergone, the least leached being Saleimoa stony sandy loam. All the types except Tiavi clay loam and Tuasivi clay loam may be considered as experiencing, roughly, the same climate. The rainfall on the soil types is Saleimoa 105–130 inches, Vaitele 110 inches, Magia 96 inches, Tuasivi 170 inches, Malatula 130 inches, and Tiavi 200 inches.

#### *Saleimoa stony sandy loam*

The profile of Saleimoa stony sandy loam is as follows:

6–9 inches	dark yellow-black-brown stony loam with good crumb structure
on	dark red-brown-yellow loose very stony sandy loam

This is the most stony soil on Upolu: here and there are heaps of jagged stones. The lava flow from which it is derived appears to belong to the Recent age. The soil is neutral in reaction. The plant-nutrient status is good, the total nitrogen content of the topsoil being abnormally high (2.01 per cent).<sup>3</sup> As judged by the growth of cocoa and coconut threes, this soil is the most fertile of the six soils studied.

#### *Vaitele stony clay loam*

The profile of Vaitele stony clay loam may be described as follows:

6 inches	dark brownish yellow stony clay loam with good crumb structure
++ feet	brownish yellow moderately compact stony clay loam.

In several localities, a dark yellowish-brown compact layer about 1 foot or more thick lies 2 feet below the surface; in others, loose brownish-yellow clay loam extends for 3 feet below the topsoil; in yet others, the soil is dark red-brown-yellow to about 12 inches below the surface. In a detailed survey, the soil containing red coloring would be mapped as a separate type. Decomposed basalt containing cores of fresh rock lies, in general, from 5 to 7 feet below the surface. Although the texture of Vaitele stony clay loam is that of clay loam, the soil and the subsoil to a depth of 2 or more feet are, like most basalt soils, very loose. The pH ranges from 6.2 to 7.0 in the topsoil and subsoil layers. The available phosphate content is, in general, decidedly low, but the nitrogen content is adequate—0.48 to 0.68 per cent. This soil is generally less fertile than the Saleimoa soil; the most fertile areas are those containing red coloring.

#### *Magia stony clay loam*

The profile of Magia stony clay loam is as follows:

6 inches	dark brownish drab stony clay loam with crumb structure
12 inches	dark brownish drab loose clay loam
to 3 + feet	dark brownish drab fairly compact clay loam.

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<sup>3</sup> Determinations of pH, available phosphate and potash, and total nitrogen were made at the Cawthron Institute, Nelson.

This soil is similar in content of available phosphate and in pH value to Vaitele stony clay loam but is less fertile.

*Tuasivi clay loam*

Tuasivi clay loam has the following profile:

3 inches dark brownish yellow clay loam, poor crumb structure  
on light brownish yellow moist compact clay loam.

In places, a compact dark brownish-yellow horizon lies at a depth of 18 inches. The subsoil is inclined to be sticky. The soil is acid (pH 5.4), available phosphate is decidedly low, and total nitrogen (0.83 per cent) is higher than that in the Vaitele soil. Available potash appears to be adequate in the Tuasivi, Magia, and Vaitele soils.

*Malatula stony clay loam*

The profile of Malatula stony clay loam is as follows:

6 inches dark brownish yellow clay loam, with crumb structure  
10 inches dark brownish yellow loose clay loam  
32 inches dark brownish yellow compact clay loam  
on 1 foot mottled black and yellow clay loam.

The compact layer is fairly general and is closer to the surface than is that in the Vaitele soils. Scattered profiles typical of the Vaitele soil occur within the areas mapped as Malatula stony clay loam. The pH of the Malatula topsoil is 5.6, and that of the subsoil ranges from 6.5 and 6.9. The content of available phosphate is decidedly low, that of potash is low, and that of nitrogen<sup>4</sup> is about equal to that of Vaitele stony clay loam. Malatula stony clay loam is the least fertile of the six soils studied, but coconuts growing on this soil have an economic life not much shorter than the average for such trees on a good soil.

*Tiavi clay loam*

Tiavi soils occur to the south of Apia on a saddle (2,254 feet) of the main range extending the length of Upolu. The profile of Tiavi clay loam is as follows:

3 inches dark black-brown yellow sticky clay loam  
19 inches dark brownish orange sticky clay loam  
6 inches dark brownish yellow compact clay loam  
on reddish brown compact clay loam.

The subsoil is lighter in color than that of any of the other soils already described. The topsoil is not darkened by humus and is difficult to distinguish from the subsoil. The pH of the topsoil is 4.9, and that of the 6-inch dark

<sup>4</sup> The carbon-nitrogen ratios for the Saleimoa, Vaitele, and Malatula soils range from 11.85 to 14.24.



brown layer is 5.8. Available phosphate is particularly low, potash is low, and the nitrogen content is about equal to that of the Vaitele soil.

#### SOIL PROCESSES

The fusion analyses given in table 1 show that the soils are losing silica, principally, and alkalis and alkaline earths, as well. The youngest soil—Saleimoa—still retains most of its lime and magnesia, but has lost a good deal of silica. With progress of leaching, more silica is lost, until only 2.5 per cent is left in the Tiavi topsoil and 1.08 per cent in the Malatula subsoil. In the most mature soils very small amounts of the alkalis and alkaline earths remain. Manganese and phosphoric acid are apparently leached out to only a very minor extent or not at all. The principal fixed constituents are alumina, iron oxide, and titania. The analyses of Vaitele and Malatula soils show that there is surprisingly little difference in composition of soil and subsoil to a depth of 5 feet, which is, in many places, the depth to decomposed rock. The only difference noted in some profiles is a higher silica content in the topsoil than in the subsoil. The silica and other soluble constituents evidently do not form a B horizon at a shallower depth than 5 feet. In the field it was thought that the compact dark subsoil horizon at about 2 feet was a B horizon, but analyses do not support this view. Further work is required to determine the reason for this compact layer.

In the extreme stages of leaching the soils are just as low in silica as are the laterites of India (2). They compare in composition with the Nipe Plateau laterite of Cuba described by Marbut (3) except that in Samoa the content of alumina is nearly equal to that of iron oxide. Also the Cuban topsoil to a depth of 1 foot contains small round iron oxide concretions.

The clay fractions of the Saleimoa and Vaitele soils, shown in table 2, have similar silica-sesquioxide ratios—between 0.42 and 0.63. Further analyses, not included in the table, gave the following ratios: two of Saleimoa soil, 0–3 and 12–15 inches, ratios of 0.58 and 0.45; and four of Vaitele soil, 0–3, 9–12, 21–24, and 25–31 inches, ratios of 0.46, 0.46, 0.45, and 0.44. Thus the weathering of basalt in Western Samoa gives rise to a clay of a composition which, insofar as its silica and sesquioxides are concerned, persists for a fairly long time while silica and other constituents are being leached out. Soils having these ratios range in reaction from neutral (young soil) to only slightly acid (in the Vaitele series). The soils that are thought to be more leached have lower ratios. In the Malatula soil the ratio drops to 0.04. At Tuasivi the ratios are 0.14 and 0.19. The topsoil at Tiavi is very acid—pH 4.9, but the subsoil—pH 5.8—is of the same acidity as that at Malatula, and the ratios are 0.12 and 0.29.

Column 1 in table 3 shows the amount of free iron oxide in the soils of four series determined by Drosdoff and Truog's method (1). It is seen that the percentage of iron in the clay fraction of two—the Vaitele and the Tuasivi—is somewhat similar, but there is a fairly large difference in the sesquioxide ratios.

TABLE 2  
*Clay fractions\**

	SALEIMOA		MAUGA, VAITELE					CROWN ESTATE, TUASIVI, SAVAI				MALATULA				TIAVI SADDLE	
	0-3'	0-12"	0-3'	9-12"	21-24"	33-36'	57-60"	0-3'	12-15'	24-27"	0-3'	33-36'	45-48'	57-60"	0-3'	23-38"	
SiO <sub>2</sub> .....	15.48	19.52	18.96	18.58	17.44	16.17	15.27	7.10	5.76	6.65	6.69	1.67	1.90	1.73	4.28	10.12	
Al <sub>2</sub> O <sub>3</sub> .....	38.09	30.51	35.24	35.79	36.04	36.24	36.42	37.20	43.51	33.23	35.46	34.77	30.61	30.24	24.98	25.43	
Fe <sub>2</sub> O <sub>3</sub> .....	28.35	34.87	37.98	38.13	38.80	39.80	40.47	42.54	40.24	47.33	47.22	51.82	54.80	54.58	56.62	52.34	
TiO <sub>2</sub> .....	6.11	6.31	5.88	6.08	6.41	6.51	6.65	8.89	8.37	10.98	8.47	10.86	11.88	12.40	12.52	11.51	
CaO.....	8.27	4.11	0.63	0.19	0.15	0.11	0.26	0.99	0.51	0.35	0.70	trace	0.06	0.04	0.63	trace	
MgO.....	1.61	3.61	0.40	0.25	0.24	0.24	0.26	1.20	0.78	0.73	0.40	0.22	0.25	0.31	0.25	0.24	
Na <sub>2</sub> O.....	0.65	0.30	0.18	0.17	0.18	0.13	0.09	0.90	0.19	0.14	0.33	0.02	0.08	0.12	0.43	0.18	
K <sub>2</sub> O.....	1.03	0.35	0.14	0.09	0.04	0.04	0.04	0.59	0.11	0.08	0.11	trace	0.02	trace	0.20	0.09	
MnO.....	0.41	0.42	0.59	0.72	0.70	0.76	0.54	0.59	0.53	0.51	0.62	0.64	0.40	0.58	0.09	0.09	
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub> .....	0.47	0.63	0.54	0.52	0.49	0.45	0.42	0.19	0.14	0.18	0.17	0.04	0.05	0.05	0.12	0.29	

\* The clay fractions were obtained by repeated sedimentation in water. The suspension was allowed to settle through a depth of 8.6 cm. for 24 hours, and the clay suspension was decanted and evaporated in porcelain on a water bath, the process being repeated until no further clay fraction could be obtained. To facilitate flocculation one or two drops of very dilute ammonia were added when absolutely necessary. In some samples 3 or 4 months were required to obtain the whole of the clay fraction.

It may be mentioned that soil erosion is not a complicating factor in the soil process. Under natural conditions there is a heavy forest cover with a thin mat of leaves. Water reaching the ground readily percolates downward. Even in the cocoa plantations where weeding is practised no erosion was noticed except on a moderate slope which was bare of fallen leaves. This is mentioned because Robinson (5) has stated that "The suggestion may be hazarded" that truncation of soil profiles during the course of time accounts for "the formation of the sesquioxidic soils of humid tropical regions."

#### USE OF THE TERM "LATERITE"

The process of leaching whereby silica is the main constituent lost is referred to as "laterization." The final stage in this process is the laterite of India, a typical section and description of which are given by Fox (2). On the surface is red or yellow clay lying on laterite consisting of bands or lenses of limonite and bauxite. The laterite lies on lithomarge (21-62 feet below the surface)

TABLE 3  
*Free iron oxide, total iron oxide, and silica in clay fractions*  
Per cent

	FREE IRON OXIDE	TOTAL IRON OXIDE	SILICA
New settlement near rubber factory, Saleimoa series, 0-3" . . . . .	22.9	28.49	17.95
Solaua, Vaitele series, 0-6" . . . . .	23.8	34.64	20.29
Vaitele, 0-3" . . . . .	20.7	35.30	21.01
Fagalie, Vaitele series, 0-3" . . . . .	26.5	38.96	15.68
Crown Estate, Tuasivi, Savaii, 0-3" . . . . .	31.2	42.54	7.10
Tiavi Saddle, 0-3" . . . . .	29.1	56.62	4.28

and kaolin which grade down to decomposed basalt. The lithomarge is a layer enriched by silica leached from the overlying soil and subsoil. A condition that is supposed to have favored the separation of iron oxide and alumina in the profile was a high ground-water level caused by the impervious lithomarge bed. A similar history for laterites in the tropics is given by Mohr, a summary of which has been published by Pendleton (4). Pendleton states that the final stage is truncation of the profile, exposing the hard ferruginous laterite, although, according to Marbut (3), in rare cases the slaggy material actually forms at the surface. Pendleton objects to the use of the term "laterite" for soils in which the process has not proceeded so far, for example, the red loam of southern United States. If truncation is not necessary or is an unimportant feature of the process we can regard the laterite as including all the profile except the B horizon in which the silica is deposited. That the term does not include the B horizon appears to be the only valid objection to its employment as a soil group name, but this does not seem sufficiently strong



to drop the term for soils like those of Samoa, when it is remembered that such usage is widespread.

#### CLASSIFICATION INTO SERIES

To divide laterites derived from basalt into soil series presents a good deal of difficulty. The following field characteristics were used in classifying:

Amount of weathering undergone by the basalt. Saleimoa soils are easily separated on this basis, and Vaitele and Malatula soils can be distinguished in this manner.

Color of soil. In similar climates the young soils show a red coloring to a depth of about 12 inches—Saleimoa and the less well-developed soils of the Vaitele series. In the areas of very heavy rainfall, the subsoil immediately below the topsoil had lost its brown coloring and taken on an orange color.

Compact layer in the subsoil. The presence of a compact layer which when moist was of darker color than the overlying subsoil was taken as evidence of greater leaching than that of a similarly colored soil in which such a layer was absent.

Compactness of subsoil. In areas of very high rainfall the subsoil is compact and sticky.

These characteristics are hardly an adequate basis for mapping out series with any confidence, as they are not constant; for example, in areas where the compact layer is present in general, there are many places where it is absent.

Recourse must be had to chemical analyses, of which the most reliable and quickest seems to be the determination of total silica. Clay fractions are of only limited use, since the silica-sesquioxide ratio in obviously young soils is the same as that in some of the older soils. A number of silica analyses were made, including some from private plantations, and it was found that the fertility as determined by crop yields was in direct proportion to the silica percentage. The analyses fitted in with the series already established and helped to place some doubtful localities. Total silica determinations will, it is concluded, be useful in determining limits for the various series.

#### SUMMARY

In Samoa the lateritic process has gone far without segregation of iron oxide and alumina.

The lateritic process is going on in a young soil which still retains most of its lime and magnesia.

Most of the soils losing silica are only slightly acid or are neutral. A very acid soil, as well, is losing silica.

In the most extreme stage the soils are just as low in silica as are many of the laterites of India.

Although some soils contain virtually only alumina, iron oxide, and titania, they are still capable of producing profitable crops for many years without fertilizers.

All the soils have a surprisingly high content of total nitrogen.

The younger soils contain red coloring, and older soils, although well drained, take on a dark brownish-yellow color.

Silica-sesquioxide ratios of the clay fractions remain constant for a fairly long period in the process—as far as the Vaitele stage. In the well-leached soils the ratio drops extremely low.

To a depth of 5 feet in the profile no marked difference occurs in total constituents or in the composition of the clay fractions.

Laterite soils derived from basalt are difficult to classify on the basis of field characteristics. All the usual chemical analyses can be utilized to assist, but obviously the amount of this work is limited on the score of expense. The determination of total silica is thought to offer the most reliable and quickest aid.

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# FERROMANGANIFEROUS CONCRETIONS FROM SOME PODZOLIC SOILS

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Concretionary matter in soils represents accumulations of secondary minerals that have been formed through the action of weathering processes. A survey of the literature indicates that concretions occur in all the soil zones from the podzol to the laterite and from the chernozem to the serozem. Ortstein and the associated "ortsteinkoerner" of the podzols have been described by Glinka (5); lime concretions are a recognized characteristic of the pedocal group of Marbut (7); Bennett and Allison (2) direct attention to the abundance of ferruginous concretions in lateritic soils.

Concretions in the extensive group of podzolic soils have been mentioned less frequently. Podzolic soils are considered to occupy that wide transition zone in humid climates between true podzols and lateritic soils. A few references that include analyses of concretions from podzolic soils indicate that Mn as well as Fe is an important constituent. Thresh (11) has noted the presence of "Mn nodules" in England; Tsukunaga (12) studied two varieties of concretions in Manchuria, the "red" being low in Mn, and the "black," high in Mn; Pelisek (8) recognized seven types of concretions in the glei soils of Moravia that contained from 1 to 15 per cent  $Mn_3O_4$ ; Zvorykin (13) working in Greece, reported 5.5 per cent  $Mn_3O_4$  in the concretions from a red soil, which is here considered to fall in the podzolic group, though the possibility of lateritic influences in that vicinity is recognized. The term "ferromanganiferous" is used, therefore, to characterize the podzolic type of concretion. This does not imply that Mn is absent from other types of concretions, but rather that it is less consistently present in significant proportions.

The presence of ferromanganiferous concretions has previously been noted in some soil types in Illinois (6). That conditions favorable to the development of podzolic soils obtain in Illinois is indicated by the climate. The average annual temperature varies from 47°F. in the north to 58° in the southern part of the state, and the rainfall varies concurrently from 32 to 45 inches. Little climatic variation is observed from east to west. The native vegetation under virgin conditions included both long grass and deciduous forest, the former giving rise to dark soils, and the latter, to light-colored soils. More detailed information about the soils of Illinois is given by Smith et al. (10).

This paper treats of the ferromanganiferous concretions occurring in Illinois

from the following three points of view: physical properties; distribution by soil type and by horizon; and composition and its relation to the composition of the total soil mass.

#### PROCEDURE

Observations on the distribution of ferromanganiferous concretions in Illinois soils have been made during the field study of soil profiles. The information so obtained was, of necessity, qualitative in nature and served chiefly to indicate the conditions under which concretions were abundant. Later, more detailed studies were made of the sand fractions obtained during mechanical analysis. The concretions so obtained were separated from the siliceous material with a magnet, and the percentages by weight were determined.

The comparison of soil and concretion composition was made on concretion specimens collected by H. J. Snider from several of the Illinois Soil Experiment Fields from which soil samples were also available. Specimens for further study were collected from definite soil types, horizons of which contained large concretions in sufficient quantity to make collection by hand feasible. Locations were chosen in widely scattered areas throughout Illinois. The specimens of concretions in surface horizons were picked up from the surface of cultivated fields. Specimens from the lower horizons were picked out of the vertical profile exposed when a hole was dug. The concretions collected ranged in size from about 6 to 1 mm., those smaller than 1 mm. being disregarded. Duplicate samples were taken from areas of the same soil type, usually several miles apart.

The relation of size to composition was studied on a sample screened from a considerable weight of soil. These specimens were separated into three size groups, and the analysis of each was made separately.

All the concretions analyzed were washed free of adhering soil particles before being ground. Standard methods of analysis were used in all cases.

#### PHYSICAL PROPERTIES

The typical ferromanganiferous concretions found in the solum of the podzolic soils in Illinois are reddish-brown to nearly black and vary in diameter from less than 0.050 mm. to more than 10 mm. Their form is usually spherical, though the surface is often roughened or irregular. Most specimens show concentric fracture when broken, thus giving evidence of a layered structure. Hardness is variable, but those specimens with the best developed fracture are usually the hardest. Inclusions of sand grains and other soil material within the concretions are numerous and give the impression that the cementing material has been deposited in the soil pore spaces. Zvorykin (13) has described concretions from Greece that have some similar properties.

Almost all the concretions examined show a slight magnetic susceptibility, though a very strong field is required to demonstrate it. Ignition greatly increases this magnetic susceptibility, as has been mentioned by Bray (3) except

in those specimens from the deeper horizons where organic matter is almost absent. The addition of a reducing agent, as sugar, will cause these concretions to become magnetic also, probably by reducing some of the  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ . Magnetization by ignition provides a convenient method for the separation of concretions from siliceous material.

When ground for analysis, the concretions yield a powder that varies from very dark brown for those high in Mn, to buff or yellow for those low in Mn.

Not all ferromanganiferous accumulations in the soil are coherent and hard enough to maintain their form when handled. The brownish splotches and the soft, easily pulverized bodies, both of which are of rather general occurrence, are of this incoherent type.

#### OCCURRENCE

Ferromanganiferous accumulations seem to be present in the solum of most soil types occurring in Illinois, either as concretions, or in the form of diffuse reddish splotches. There are great differences, however, in the relative abundance and size of concretions, not only between different types, but also between the several horizons of the same profile. Field observations over a period of years have indicated that certain environmental and soil features are associated with the presence of large concretions in appreciable numbers. The most important of these features are the following:

1. Poor drainage.—In surface horizons this is usually associated with level topography.

Light-colored soils.—In general, soils that have been subjected to considerable degradation.

Solonetz-like soils.—Slick spot conditions described by Smith (9). This situation is unusual in that calcareous, as well as FeMn concretions are abundant, whereas the solum of most Illinois soils is leached of  $\text{CaCO}_3$ .

These observations are interpreted to mean that most pronounced concretion formation is correlated with intensive or prolonged weathering, with the slow removal of the end-products of weathering from the profile, and with the frequent alternation of reducing and oxidizing conditions in the soil. Similar conditions are implied by Zvorykin (13) and by Pelisek (8) when they point out that concretions are found in soils frequently subjected to a high water table.

Certain "pipestems" in loess and the irregular masses which appear to be formed by ground-water action represent ferromanganiferous segregations that are frequently encountered. Since these concretionary forms probably are not directly concerned with soil processes, they will not be discussed here.

In the course of mechanical analysis the sand fraction is separated by an approximately 0.05-mm. screen. Concretions of this size and larger are thus retained with the other coarse material, from which they may be separated with a magnet after gentle ignition, as has been described. In this way it is possible to determine the percentage of concretions larger than 0.050 mm. in a given sample of soil.

The sand fractions of many hundreds of samples have been examined for concretions, which were found to be present almost without exception, though the relative abundance varied tremendously. The samples represented a wide range in soil characteristics, including virtually all conditions prevalent in Illinois with the exception of the group of coarse sandy soils of restricted distribution. It is possible that very sandy profiles might not contain concretions, since their good drainage would facilitate the removal of what little secondary material was formed.

A surprisingly large number of the concretions found with the sands were very small. Some of these may be fragments of larger concretions that had been broken during the preparation of the soil for mechanical analysis, but many of the small specimens examined showed no fracture, and, on the contrary, possessed rather smooth, rounded surfaces, indicating that they were genetic units.

The extreme scarcity of large specimens in most soils explains why ferromanganiferous concretions are overlooked in many field descriptions of soil

TABLE 1  
*The concretion content of some surface soils*

SOIL		CONCRETIONS
		<i>per cent</i>
West Salem Experiment Field	Plot 105 . . . . .	5.5
	106 . . . . .	5.6
	107 . . . . .	5.9
	108 . . . . .	6.2
Sparta Experiment Field Plot 205A . . . . .		5.5

profiles. The concretions in well-drained soils generally do not exceed 1 mm. in diameter and thus are not easy to discover; consequently, they were formerly thought to be absent in such soils in Illinois. Similarly in most dark-colored prairie soils, field observations usually fail to detect the concretions present.

Table 1 gives the percentage of concretions found in the surface of some highly weathered, level soils containing heavy claypans that impede drainage. Locally, farmers call these soils "buckshot" land because of the abundance of large concretions found on plowed fields. The variation in the concretion contents of these soils from West Salem and Sparta is less than might be expected. Though 5 to 6 per cent of concretions is not high compared to contents up to 38 per cent reported by Bennett and Allison (2, p. 360) for lateritic soils, yet it represents a considerable segregation of ferromanganiferous material for podzolic conditions. Tsukunaga (12) found only 2.8 per cent of concretions in the Manchurian soil he studied.

The concretion percentages by horizons are given in table 2 for two complete profiles, both highly weathered forest soils, one of which (Ava) is well drained,

and the other (Wynoose), poorly drained. Both show, in general, a decrease of concretions with depth. A parallel observation was made by Tsukunaga (12) for a Manchurian soil, which had 2.8 per cent in the upper 50 cm. and only 0.4 per cent at a depth of 150 to 200 cm. The upper horizons of most soils should probably contain more, as well as larger, concretions, since this part of the profile has undergone greatest weathering. The Wynoose, however, has slightly more concretions from 30 to 43 inches than in the horizons either immediately above or below, which substantiates a field observation that concretions seem to be more abundant in definite layers or zones in some profiles.

The higher percentage of concretions in the poorly-drained Wynoose when compared to similar horizons of the well-drained Ava is in agreement with the

TABLE 2  
*The distribution of concretions in two profiles*

AVA SILT LOAM			WYNOOSE SILT LOAM		
Laboratory Number	Depth	Concretions	Laboratory Number	Depth	Concretions
	<i>inches</i>	<i>per cent</i>		<i>inches</i>	<i>per cent</i>
15091	0-6	1.9	15051	0-4	3.4
15092	6-10	1.2	15052	4-9	2.6
15093	10-14	1.0	15053	9-13	2.9
15094	14-17	0.7	15054	13-18	2.5
15095	17-20	0.6	15055	18-21	1.4
15096	20-23	0.8	15056	21-24	1.2
15097	23-25	0.6	15057	24-27	1.0
15098	25-28	0.7	15058	27-30	1.0
15099	28-31	0.5	15059	30-34	1.5
15100	31-34	0.5	15060	34-39	1.5
15101	34-38	0.5	15061	39-43	1.6
15102	38-42	0.7	15062	43-50	1.0
15103	45-50	1.0	...	...	...

general observation that poor drainage is associated with a greater abundance of concretions.

#### CHEMICAL COMPOSITION

Further justification for the term "ferromanganiferous" suggested above will be apparent from the following data on composition. In table 3 are presented fusion analyses of some concretions and of the soils from which the concretions were collected. In general, the concretions are much higher in  $Mn_2O_4$  and  $Fe_2O_3$ , a little higher in  $Al_2O_3$ , and lower in both  $SiO_2$  and carbon than the soils in which they were found. The segregation of manganese, in particular, is noteworthy, more than 50 times as much being in these concretions as in the corresponding soil.

The summation column of Table 3 indicates that 2 to 4 per cent of the



constituents are unaccounted for. Of the unreported constituents,  $P_2O_5$  and  $TiO_2$  precipitate with the  $Al_2O_3$  and so are included in the totals with this fraction. Qualitative tests indicated that  $CaO$ ,  $MgO$ ,  $K_2O$ , and  $Na_2O$  are present in about the same proportions as in soil. As was mentioned under "Physical Properties," soil material is imbedded throughout the concretions, and therefore the usual minor constituents of soils will also be present in the

TABLE 3  
*Analyses of some soils and concretions therefrom*

SAMPLE		IGNI- TION LOSS	$SiO_2$	$Mn_2O_4$	$Fe_2O_3$	$Al_2O_3$	SUMMA- TION	ORGAN- IC CARBON
		per cent	per cent	per cent	per cent	per cent	per cent	per cent
West Salem Plot 105	Soil	4.8	79.6	0.14	3.0	8.7	96.2	0.91
" " " "	Concretions	11.0	50.7	11.3	14.0	11.3	98.3	0.38
West Salem Plot 109	Soil	4.7	81.6	0.12	2.8	7.9	97.1	1.06
" " " "	Concretions	10.1	50.1	6.6	21.1	9.4	97.3	0.42
Sparta Plot 205A	Soil	3.3	82.8	0.16	1.8	7.7	95.8	0.61
" " "	Concretions	9.6	50.4	11.5	15.8	10.6	97.9	0.27
Carlinville Plot 405	Soil	7.0	76.4	0.06	2.6	9.0	95.1	1.80
" " "	Concretions	10.3	46.6	3.6	24.3	10.7	95.5	0.56

TABLE 4  
*Analyses of concretions from certain soils*

SOIL TYPE	HORI- ZON	LABO- RATORY NUMBER	IGNI- TION LOSS	$SiO_2$	$Mn_2O_4$	$Fe_2O_3$	$Al_2O_3$	SUMMA- TION	ORGAN- IC CARBON
			per cent	per cent	per cent	per cent	per cent	per cent	per cent
Wynoose silt loam	A <sub>1</sub>	b428	9.8	54.6	13.2	9.0	11.2	97.8	0.33
" " "		b535	9.2	53.2	13.1	11.6	10.7	97.8	0.44
Rushville silt loam	A <sub>1</sub>	A793	10.2	51.9	11.1	14.0	10.5	97.7	0.88
" " "		A237	12.0	39.0	8.8	27.2	11.0	98.0	..
Putnam silt loam	B <sub>1</sub>	b344	9.6	50.2	6.7	18.1	11.9	96.5	0.27
" " "		b856	9.0	53.2	7.7	13.8	12.2	95.9	0.00
Grundy clay loam	B <sub>2</sub>	b121	10.6	47.8	7.0	21.0	10.9	97.3	....
" " "		A391	10.5	49.2	9.2	17.9	10.9	97.7	0.54
Denny silt loam	B <sub>2</sub>	A113	9.5	50.0	8.1	16.8	12.1	96.5	0.24
Illinoian gumbotil	B	A846	10.3	46.2	10.3	17.8	11.8	96.4	0.12
"Pipestem" from loess		13	10.5	43.8	3.2	30.4	7.9	95.8	0.59

concretions. A complete analysis of a soil similar to that at West Salem is given by Brown, Rice, and Byers (4, p. 31) and is indicative of the unreported constituents to be expected in the concretions.

Organic matter was found by Aarnio (1) to be important in some types of ortstein formation. The fact that the concretions contain less than half as much organic matter as do the soils (table 3) indicates that the organic matter is of minor importance, at least in these samples. The high ignition losses probably represent water associated with the  $Fe_2O_3$  of the concretions, since

the organic matter content is less than 1 per cent (assuming the usual factor of 1.7 to convert carbon to organic matter).

Significant variations that are not related to the soil composition occur in the composition of the concretions reported in table 3. Further evidence on this point can be deduced from the analyses of a number of additional samples collected from soil types widely distributed throughout Illinois (table 4). They all show the marked concentration of Mn and Fe, the high ignition losses, and the low carbon content that characterized the concretions of table 3. The marked similarity of the composition of all samples suggests that local conditions are of less significance in the formation of these concretions than are general weathering processes common to the region. For example, there is more difference between the two samples from the Rushville surface than there is between samples from different horizons and from different soil types. Further, the sample from the gumbotil, which is a B horizon developed before the advent of the Wisconsin glaciation, has nearly the same composition as one from the Grundy B horizon, which developed on material of Wisconsin age.

TABLE 5  
*Relation of size of concretions to their composition*

SOURCE OF SAMPLE	DIAMETER OF SPECIMENS	IGNITION LOSS	SiO <sub>2</sub>	Mn <sub>2</sub> O <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SUMMA- TION
	mm.	per cent	per cent	per cent	per cent	per cent	per cent
Ewing Soil Experiment Field Plot 310	>2	10.3	46.3	8.3	22.4	10.4	97.7
	2 to 1	10.6	48.3	2.0	26.3	10.0	97.2
	1 to 0.3	11.0	50.3	1.4	24.4	10.7	97.8

"Pipestems" in loess appear to have been formed in old root channels, for they possess a concentric cylindrical structure that is difficult to explain in any other way. Their wide occurrence lends interest to their properties, and on this account one analysis is included in table 4. Though somewhat lower in Mn and Al than are the soil concretions, it exhibits in general a similar composition.

A definite relation seems to exist between size and composition of concretions in some instances. The data in table 5 illustrate this for one sample. The chief variable is the content of Mn, which shows a steady decrease with diminishing size, while Fe tends to increase, but less consistently. More data are needed to determine how general the correlation between size and Mn content may be.

#### SUMMARY

Field and laboratory studies have been made of the FeMn concretions occurring in the podzolic soils of Illinois. The results are presented under three headings, as follows:

**Physical properties.**—The concretions examined were irregularly spherical, dark brown, moderately hard bodies that varied in size from 10 mm. to less than 0.05 mm. They become magnetic after gentle ignition.

**Occurrence.**—In general, concretions were found to be most abundant in the surface horizons of poorly-drained, light-colored soils, though a few small ones were present in virtually all horizons of nearly every soil type.

**Composition.**—The concretions were found to be much higher in Mn and Fe, slightly higher in Al, and lower in  $\text{SiO}_2$  and organic matter than were the soils in which they occurred. Large concretions were found to be higher in Mn than were small ones.

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# THE PRESENCE OF TITANIA IN CHEMICALLY UNWEATHERED SOILS

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Joffe and Pugh (7), who have investigated the titania content of many different soils, are of the opinion that the chemical soil-forming processes are the cause of the differences noted. This may be true of the soils investigated, but surely under other climatic conditions soils exist in which the differences in the contents of titania are due to another, purely mechanical, process.

According to the oldest published investigations, the texture of the soil and the content of titania seem to be dependent upon each other. This is evident although the classification is not based directly upon the mechanical composition of the soils.

Dunnington (3) determined the titania content of 72 soils, of which 40 were from the United States, and the rest were from different parts of the world. The textural composition of 31 samples was designated. Of these samples, 19 were clays, 10 loams, and 2 sands. The average percentages of titania in these three different textural groups were as follows: clay, 1.38; loam, 0.77; sand, 0.20.

Dunnington is of the opinion that iron and titania are found simultaneously in soils because titania is contained in ilmenite, one of the commonest rock minerals. In soils having a low content of iron, he thinks, the titania occurs as titanite.

Robinson (9) investigated 26 soil samples from the United States and determined titania in all of them. According to the chemical analyses, the soils investigated are quite different from the soils of Finland, and the chemical theory of the enrichment of titania in these soils may, therefore, be true. The following tabulation shows, however, that the titania content of the fine-textured soils is higher than that of the coarse-textured soils:

SOIL	NUMBER OF SAMPLES	TITANIA CONTENT
		<i>per cent</i>
Clay.....	2	1.08
Clay loam.....	2	1.22
Silt loam.....	8	0.72
Loam.....	5	1.14
Sandy loam.....	6	0.71
Stony loam.....	2	0.75
Fine sand.....	1	0.60

Silt loam seems to be an exception to the general rule, but this may be explained by mechanical analyses, which show that the clay fraction in silt loam was the smallest determined.

Robinson thinks that the titania occurs as rutile or rutile inclusions in quartz. He has noticed, however, that the amount of quartz in fine fractions is smaller than that in coarse fractions, and it may be supposed that this is true also for soils of fine texture. The mineralogical investigations of sand and silt fractions show that the quantity of muscovite is higher in every sample of silt than in the two sand fractions separated. The relation between texture and titanium content is expressed very clearly by Geilmann (5), who after an investigation of 30 samples, came to the following conclusions:

The clays are the richest in titania, the content of which reaches 1 per cent.

The quantity of titania in loam and silt soils is smaller, followed by that in sand and calcareous soils.

Pure chalk and sand contain very small quantities of titania.

No sample has been found quite free from titania.

The same conclusions can be drawn from the aforementioned investigations, as well as from the investigations of Robinson et al. (10, 11) and of Joffe and Pugh (7). The last mentioned scientists have observed that soils rich in iron also contain titania in greater quantities than do soils of low iron content. They are of the same opinion as Dunnington that the titania is contained in ilmenite, thinking that ilmenite is formed anew, especially in the B horizon, during the process of podzolization. Another compound that would explain the presence of titania is  $\text{Ti-Ti}(\text{HPO}_4)_2$ . Joffe and Pugh ascribe the variations in the contents of titania to the weathering processes of soils. It is also quite natural that titania as well as iron can move from one place to another and be enriched through podzolization in the B horizon or through the laterization process.

The purpose of this investigation is not, however, to try to explain the vicissitudes of titania in the soil-forming processes. The discussion deals rather with the original titania content of soils as they are formed through the action of the sea in such countries as Finland, which has risen from the sea in the course of many thousands of years and of which the finer homogeneous soils at least are formed through the action of waves along the beaches of seas and lakes (13). As this process of soil formation involves the grinding of unweathered rock material and takes place very rapidly, the soils are formed in Finland and in the Scandinavian Peninsula in the same manner as are those in northern Russia where the common rock minerals form the soil, namely, from undecomposed rock material of different degrees of fineness. The original mineral composition of the rocks has naturally been changed during the wearing and sedimentation processes; some minerals have decreased and even disappeared, and others have increased according to such individual properties as specific gravity, hardness, and cleavage.

As the soil-forming processes in Finland are not very significant, the possibilities of following the primary characteristics of soils are very good.

For the present purpose, it must be remembered that all the aforementioned titania minerals are of such hardness and specific gravity that their enrichment in mechanical sediments is not easily explained. Although ilmenite is one of the commonest minerals in rocks, its enrichment cannot be explained on the grounds already set forth. Its specific gravity is between 4.5 and 5.0, and its hardness is the same as that of quartz. As quartz is one of those minerals the quantity of which is decreased in the course of the grinding and sedimentation processes, the increase of ilmenite during the same processes is improbable. The same holds true for other titania minerals, such as titanite and rutile. Although titanite is softer and lighter than the other titania minerals, its density, 3.5, exceeds the densities of common soil-forming minerals by one unit. Thus it seems improbable that the increase of titania in the above soils depends on the concentration of these titania minerals during the grinding and sedimentation processes.

All that has been said naturally holds true only when the mechanical sediments are considered. In other soils, other processes may prevail, and the increase and decrease of titania may depend upon them.

During the mechanical processes which have ground and sedimented the soils here in question, one of the main features of the change in mineral composition is the increase of micas in soils as the average diameter of the grains decreases—an observation first made by Atterberg (1). Mica is a little heavier than quartz and the feldspars, but its softness and its capacity to float in water, depending upon its cleavage into thin and comparatively broad tables, account for the increase of this mineral. I have shown in a previous publication, through calculations based on the chemical composition of Finnish clays, that the mica content of such clays must be very great (12). Furthermore, röntgenographic investigation has shown that the mica content of mechanical clays may be very high.

As the continual increase of micas in Finnish clays seems to be proved, it is of interest to try to explain the increase of titania on this basis. Micas and amphiboles are the two groups of titania minerals which may be encountered in clays. The increase of amphiboles is hampered, however, by their hardness and comparatively high density, 3.0–3.5. The feldspars and the quartz are free from titania. The content of titania in micas, on the contrary, is very high. The analyses of micas, published by Iddings (6), show a range in titania content from 1 to 5 per cent; in lepidomelanes the range is from 2.61 to 4.73 per cent. In many Finnish rocks the micas are of the last-mentioned type. The micas of clays are generally considered to be muscovites, the titania content of 13 samples of which was found by Doelter (2) to range from 0.11 to 3.94 per cent, averaging 1.30 per cent. The titania content of Finnish biotites, according to Lokka (8), averages 2.5 per cent, one biotite being free from titania.

These quantities of titania in micas readily explain the titania content of Finnish clays, which generally ranges from 0.5 to 0.8 per cent. The quantity of micas in clays calculated by me ranges from 20 to 50 per cent, and the quantity of titania increases simultaneously with the calculated increase of micas.

The average titania content of 27 Finnish clays was calculated to be 0.68 per cent. These clays include many different kinds, from coarse loamy clays to the very stiffest clays in which the fraction under 0.002 mm. amounts to 90 per cent. The average titania content of 12 sand samples was 0.40 per cent.

The best test for the increase of titania together with the micas is, however, the observation that when a mechanical analysis of a clay is made, the titania is found in greatest quantities in the finest fraction. An example is given in the following analysis of a Finnish clay (12), together with an analysis of the finest fraction (under 0.002 mm. diameter) of the same clay, calculated on the water-free and humus-free basis:

	ORIGINAL CLAY	0.002-MM. CLAY FRACTION
	<i>per cent</i>	<i>per cent</i>
SiO <sub>2</sub> .....	65.24	59.22
TiO <sub>2</sub> .....	0.77	1.14
Al <sub>2</sub> O <sub>3</sub> .....	15.79	20.23
Fe <sub>2</sub> O <sub>3</sub> .....	2.92	4.90
FeO.....	3.37	1.84
MnO.....	0.08	0.08
MgO.....	2.27	4.05
CaO.....	2.66	1.99
Na <sub>2</sub> O.....	3.72	3.96
K <sub>2</sub> O.....	3.01	2.49
P <sub>2</sub> O <sub>5</sub> .....	0.17	0.09
Total.....	100.00	99.99

The increase of titania in the fraction under 0.002 mm. as compared with the titania present in the original clay has been very great, and the explanation that the titania has been increased together with the micas is plausible. If titania were in the clay in the form of some weathering product, it would be concentrated in coarser fractions because of its high specific gravity.

One of the best examples of the increase of titania in clays is reported by Tamm (16). He ground very fine a granite, the mineralogical and chemical composition of which had been thoroughly investigated. The fine powder was treated for 12 hours both with water containing carbon dioxide and with common distilled water. The clay fraction of each of three samples was separated and analyzed, all three analyses being of about the same general character. Although the granite used contained only 0.89 per cent titania, the titania in the clay fraction averaged 2.40 per cent. The titanite content

of the granite was 0.34 per cent; therefore only 0.14 per cent of the total titania occurred in the titanite. The hornblende content of the granite was 7.64 per cent; therefore the hornblende contained 0.11 per cent of the total titania, for, according to Sundius (15) the titania content of the hornblende was 1.47 per cent. The titania content of micas must be, therefore 0.64 per cent; accordingly, the greatest part of the titania in the rock itself was in micas. As the quantity of titania in the clay fraction is about three times as high as that in the rock, it is evident that the increase of titania must be due primarily to the increase of micas during the sedimentation process in this experiment. Because of the very short duration of the experiment, changes of these dimensions cannot be ascribed to chemical reactions. The  $\text{Al}_2\text{O}_3:\text{TiO}_2$  ratio of the clay and that of the calculated mica seem to bear out these conclusions, for the ratios are almost equal, the former being 6.25, and the latter, 6.43.

The artificial clay fraction of Tamm differs in many ways from the clay fraction separated from the aforementioned Finnish clay. This may be because the natural sedimentation process separated the different minerals much more thoroughly than did the comparatively short artificial separation. It must also be kept in mind that the granite used by Tamm contained no muscovite, which is considered to be the main constituent of the clay micas.

The foregoing experiments show that the increase of titania in these artificial clay fractions or separates can be explained only as a result of the increase of the micas. The titania content of clay minerals is very low, according to the analyses of Engelhardt (4). The quantities of titania in the different groups of clay minerals are as follows:

CLAY MINERAL	NUMBER OF SAMPLES	TITANIA CONTENT
		<i>per cent</i>
Kaolinite and anauxite .....	10	0.46
Dickite .....	1	trace
Halloysite and metahalloysite .....	..	....
Montmorillonite .....	5	0.50
Beidellite .....	1	0.84
Nontronite .....	4	0.04
Clay minerals rich in magnesia .....	1	0.44

The titania content of all these minerals seems to be so low that the high titania content of mechanical sediments cannot be explained by the presence of larger quantities of these minerals.

One other observation makes improbable the theory of the increase of titania through chemical weathering in clays of mechanical origin. The general occurrence of titania in chemical combination with iron leads one to suppose that if titania were in the form of weathering products in the clays in question the presence of iron would also be probable. The characteristic red-brown color of iron is not found, however, in Finnish clays under the generally thin



layer which lies above the ground water and in which only very slight weathering of the clay can be discerned. It is only after our clays have been heated to 400 or 500°C. that the first faint tinge of iron can be observed, and at these temperatures the decomposition of silicates begins, and iron can be found in the form of oxide. As it must, accordingly, be certain that iron is not originally present in the form of hydrates or oxides or in any other form of hydrolytic decomposition, it is impossible to believe that titania should be increased in this manner. Among the many kinds of clays are some that contain iron in the form of hydrolytic decomposition products, but the iron in these clays occurs in greater quantities (14) in the coarse fractions than in the fine fractions, a phenomenon not encountered in mechanical clays.

#### SUMMARY

Investigations, both old and new, have demonstrated that the titania content and the textural composition of soils are dependent upon each other, in that fine-grained soils contain more titania than do coarse-grained soils.

As the common titania minerals are hard and have a very high density, their enrichment, especially in mechanical sediments, is highly improbable.

In mechanical sediments the only minerals that can explain the variations of titania are the micas.

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## ISOHYDRIC pH VALUE OF SOILS AND ITS DETERMINATION

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Problems connected with soil reaction and related phenomena constitute one of the most important branches of soil science. Methods of measuring the pH value of soils have received considerable attention, and some of these have attained a high degree of refinement and precision. The weak point in all these methods lies in the very nature of things. A soil suspension behaves like an ordinary buffer solution, but the analogy is not complete insofar as the one is a heterogeneous and the other a homogeneous system. In an ordinary buffer solution, the hydrogen and the hydroxyl ions are uniformly distributed throughout the liquid mass; whereas in a soil suspension, they are confined to the portion of liquid immediately in contact with the surface of the particles and can be easily filtered off. Under such conditions, it is doubtful whether we are justified in speaking about the pH value of soils without reference to the arbitrarily fixed conditions under which the actual measurements were carried out. On theoretical grounds, every soil should have a fixed pH value determined entirely by the amount and nature of exchangeable bases in it. The pH value of the soil should, therefore, be a fundamental constant not subject to rapid variations. Actually our methods of measurements give a value which fluctuates with alterations in the experimental conditions. Need was, therefore, felt for an absolute measure of the pH value of soils and other related phenomena. This paper deals with such a method.

The investigation was originally started from theoretical considerations, as it was thought that modern electrical methods of pH determination are sufficiently simple and quick that it would be difficult to replace them by a chemical method for ordinary routine work. The chemical method, however, entailed a procedure that afforded so much other information which is useful in any soil investigation, that the method could be recommended for inclusion in routine soil examination. In order to distinguish from other methods of determining soil reaction, the isohydric pH value of a soil may be defined as the pH value of a buffer solution which shows no change in reaction on coming into contact with the soil. Mattson<sup>1</sup> has called this pH the point of exchange neutrality.

<sup>1</sup> Mattson, Sante 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 343.

## EXPERIMENTAL

The starting point of this investigation was the following assumptions:

A fully unsaturated soil behaves like an acidoid with a well-defined titration curve.

The pH value of every soil in nature represents a single point on its titration curve governed by the state of its neutralization with bases. It is, therefore, a buffer mixture of a definite proportion of acidoid-saloid, which determines its pH value.

Soil if shaken with a buffer solution will have its acidoid-saloid equilibrium point shifted toward that of the buffer solution. In other words, it will take the basic portion from a buffer solution of higher pH value and give its basic portion to one with a lower pH value than that of itself. Consequently, when no change occurs in reaction, the soil and the buffer are isohydric, i.e., the pH value of the soil is equal to that of the buffer solution.

It is to be remembered that when a soil is shaken with water, it hydrolyzes, and a part of the exchangeable base goes into solution as hydroxide. Since the amount of the hydroxide going into solution depends on the state of saturation or pH value of the soil, and since the actual amount of the base removed from the soil and going into solution is very small, the pH value of the water approximates that of the soil. In natural soils, however, this ideal condition is seldom attained. There is always some salt present, which can suppress this hydrolysis, thus resulting in an increase in the H-ion activity or a lowering of the pH value. The ideal method, therefore, would be the one in which no hydrolysis is allowed to take place. In the isohydric method, this state of affairs is realized by interpolation, for, by definition, the isohydric pH value represents the pH value of that buffer solution which undergoes no change when coming into contact with the soil. This situation can exist only when the pH value of the soil is equal to that of the buffer solution; if the reaction of the buffer and that of the soil are different, some change must inevitably take place, resulting in the transfer of the base from one to the other. In short, the isohydric method depends not on a single measurement, but on a series of titrations from which the buffer in which the soil would undergo no change is determined; an absolute measure of the pH value of the soil is thus obtained. All other methods must involve some change in the base content of the soil; however small this change may be, it must affect the pH value of the soil. Although this change may not be material, from the practical point of view, its theoretical significance must be recognised.

The problem of finding isohydric pH values resolved itself, in the first instance, to the choice of a series of buffer mixtures, the acid-salt proportion of which could be easily ascertained and any change readily detected. Boric acid-borate and acetic acid-acetate mixtures proved useful for the purpose; the former covered the range between pH 7.8 and 10, and the latter between pH 3.7 and 6.

A mixture of acetate-acetic acid or of borate-boric acid could be easily analyzed by titrating with standard acid, and the pH value of any mixture could be ascertained from the titration curve. In tables 1 and 2 are given pH values of K-acetate-acetic acid and K-borate-boric acid mixtures. These

data, when plotted, give smooth curves from which any intermediate value can be interpolated. Thus any change in the pH value of these buffers can be measured by titrating before and after shaking with the soil. Since any increase or decrease in the basic portion of the buffer is brought about by a corresponding change in the exchangeable base content in the soil, and since the pH value of the soil and that of the buffer have been equalized by shaking, the final pH value of the mixture, as determined by titration and interpolation from the curve, gives the pH value of the soil resulting from a certain change in its base content, which, in turn, is given by the change in the acid titration value of the buffer on shaking with the soil. Thus by using a series of buffers, a number of values are obtained representing increasing changes in the exchangeable base content and the corresponding changes in the pH value of the soil. These values when plotted give a smooth curve, which may be called the isohydric titration curve of the soil. From this curve

TABLE 1  
*Composition of acetate-acetic acid buffers and their pH values*

pH. ....	3.72	4.05	4.27	4.45	4.63
Acetic acid, 0.2 N .....	90	80	70	60	50
K-acetate, 0.2 N .....	10	20	30	40	50

TABLE 2  
*Composition of boric acid—KCl—KOH buffers and their pH values*

25 cc. of 0.2 N boric acid and 0.2 N KCl mixture + x cc. of 0.2 N KOH diluted to 100 cc.

pH. ....	7.8	8.0	8.2	8.4	8.6	8.8
KOH (x) .....	1.32	2.0	2.95	4.27	6.0	8.2
pH. ....	9.0	9.2	9.4	9.6	9.8	10.0
KOH (x) .....	10.7	13.35	16.0	18.425	20.4	21.95

is interpolated the pH value of the buffer which would undergo no change in its titration value. Since at this point the soil obviously would undergo no change in its base content either, this point represents the isohydric pH value of the soil. From the isohydric titration curve, the buffer capacity of the soil is obtained by noting the change in its base content required to produce a unit change in pH value. The lime requirement of the soil to any pH value could be easily obtained from the same titration curve.

For standardizing the working conditions of the method outlined, the following preliminary determinations had to be made:

- Effect of time of shaking on the equilibrium between soil and buffer solution.
- Effect of soil-buffer ratio.
- Fate of the borate ion.

The results of these preliminary experiments showed that equilibrium is attained in 2 hours, longer shaking up to 48 hours making no appreciable

difference; soil-buffer ratios ranging from 1:20 to 1:5 gave practically the same result; and the concentration of the borate ion remained the same before and after shaking of the buffer with the soil.

#### DETAILED DESCRIPTION OF THE METHOD

Stock solutions of potassium acetate-acetic acid and potassium borate-boric acid of the following pH values are made: 4, 5, 6, 8, 9, 10. Two hundred

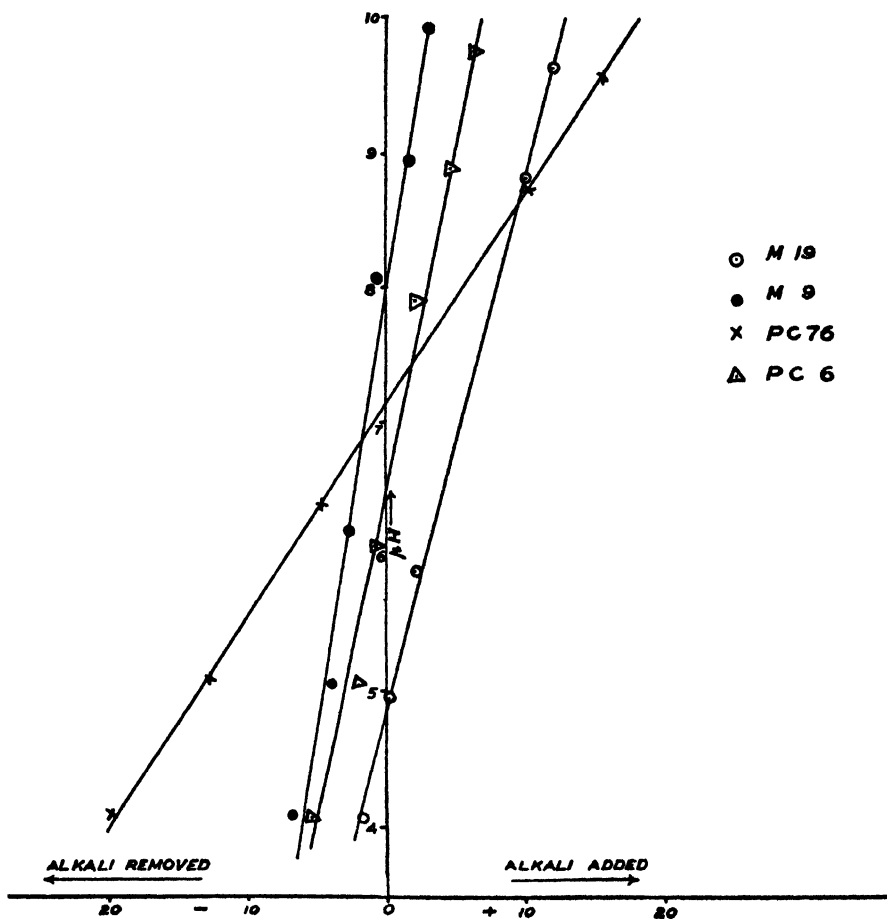


FIG. 1. ISOHYDRIC TITRATION CURVES OF SOILS

cubic centimeter portions of these solutions are shaken for 2 hours with 10-gm. portions of the soil, and the suspensions are filtered. The filtrates are titrated with standard acid, methyl orange being used as indicator. For the amount of acid required, the pH value is read from the curve. Assuming that when the state of equilibrium is reached, the soil and the buffer are isohydric with respect to hydrogen-ion concentration, and assuming that

**TABLE 3**  
*The pH values of various soils by different methods*

SOIL NO.	ANTIMONY ELEC- TRODE, pH VALUE	QUINHYDRONE, pH VALUE	ISOHYDRIC, pH VALUE	BUFFER CA- PACITY	CLAY CONTENT	BUFFER CAPAC- ITY PER 100 GM. OF CLAY
				<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>
1	7.3	7.39	6.8	3.0	32.2	9.32
2	7.5	7.26	7.3	2.6	13.76	18.9
3	7.6	7.4	7.5	2.4	20.6	11.66
4	7.6	7.59	7.65	2.2	8.7	25.28
5	7.9	7.94	7.95	4.0	11.46	34.90
6	8.1	8.07	8.6	5.0	16.0	31.26
7	7.9	8.06	8.4	3.4	13.9	24.46
8	7.5	7.36	8.0	5.2	29.8	17.44
9	7.6	....	8.02	2.8	9.26	30.24
10	7.0	7.27	6.9	4.0	25.26	15.84
11	7.5	7.69	8.1	3.6	19.1	18.84
12	6.8	7.09	6.65	4.4	18.34	24.0
13	7.3	7.13	7.3	2.4	8.98	26.72
14	7.6	7.42	7.05	2.4	15.8	15.18
15	7.7	7.86	8.0	3.0	25.68	11.68
16	7.8	....	8.3	2.4	5.84	41.1
17	6.7	6.08	6.6	2.0	14.6	13.7
18	5.6	6.08	5.0	4.0	33.28	12.02
19	5.9	.	4.85	5.2	27.76	18.74
20	7.5	6.67	6.55	2.0	20.72	9.66
21	7.8	.	7.8	2.6	8.94	29.08
22	8.0	7.31	7.6	4.2	2.32	181.04
23	8.0	7.20	7.65	3.6	16.32	22.06
24	7.5	7.19	7.5	1.4	8.86	15.8
25	8.0	7.64	7.75	4.2	15.42	27.24
26	7.7	6.98	6.65	2.8	19.58	14.3
27	7.7	7.81	7.75	2.4	11.96	20.06
28	7.2	7.38	7.0	2.0	11.9	16.8
29	7.7	8.24	7.6	3.0	10.88	27.58
30	7.0	7.33	6.8	3.2	18.78	17.04
31	6.5	7.26	6.85	2.0	8.32	24.04
32	7.0	7.44	7.0	2.6	22.9	11.36
33	7.6	8.32	8.45	3.6	15.98	22.52
34	5.1	5.12	5.05	2.4	6.9	34.78
35	5.2	5.26	5.15	2.8	22.84	12.26
36	5.2	5.05	5.05	2.8	5.38	52.04
37	6.6	7.68	8.05	5.6	8.02	69.82
38	7.6	7.69	7.09	2.8	9.56	29.28
39	7.1	7.43	7.5	2.2	12.8	17.18
40	5.2	....	5.4	5.2	47.04	11.06
41	5.8	....	5.85	5.6	48.32	11.58
42	5.7	6.48	5.7	5.0	19.1	26.18

*Humus soils*

		GLASS ELECTRODE				
76	...	6.7	7.18	13.2	31.04	42.52
78	...	6.49	6.6	4.6	28.30	16.26
79	...	6.39	6.65	3.0	28.98	10.36
81	...	6.95	7.35	14.0	44.22	31.66
86	...	6.4	6.3	8.6	30.48	28.22
87	...	6.33	6.35	9.2	33.68	27.32



the base lost or gained by the buffer represents a gain or loss by the soil, we know the gain or loss of base by the soil in reaching the isohydric pH value. Thus a series of values corresponding to the series of buffer solutions are obtained, which when plotted, give a smooth curve, from which the pH value corresponding to no change in the buffer is interpolated. The acetate-acetic acid buffers evidently could not be used for calcareous soils. For these, borate-boric acid buffers alone are suitable, and only the upper portion of the curve is obtained. The buffer capacity of the soils, which may be defined as the milligram equivalents of alkali per 100 gm. of soil required to produce a change of 1 unit on the pH scale, is easily read off the isohydric titration curve. The lime requirement of acid soils to any pH is calculated from the interpolated

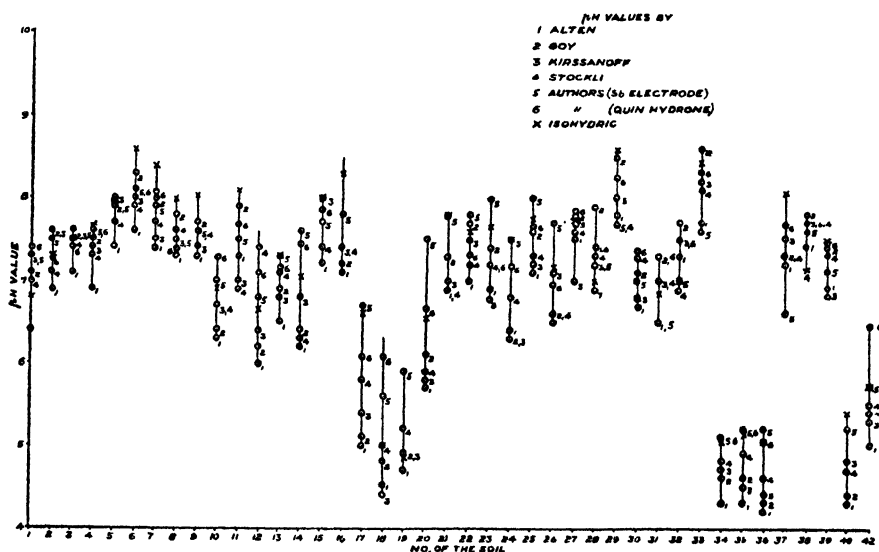


FIG. 2. THE pH VALUES OF SOILS AS DETERMINED BY DIFFERENT WORKERS AND BY DIFFERENT METHODS

value of the base equivalent corresponding to the desired pH value. A number of typical isohydric titration curves of soils are given in figure 1. It will be seen that most of the soils give a straight line relationship throughout the entire titration curve. In some cases, however, there is a slight curvature in the lower part of the curve, which is due to the presence of  $\text{CaCO}_3$  in the soils. This curvature, however, does not affect the interpolation.

#### COMPARISON WITH OTHER METHODS

The difficulty of measuring the pH value of soils by the usual methods has already been pointed out. The agreement between the soil reaction determined by any of the standard methods and the isohydric pH value, therefore, can only be approximate. For comparison, the pH values were determined

in 1:5 soil-water ratio with the antimony electrode as well as with the quinhydrone electrode after shaking for 1 hour. The results are given in table 3. The pH values of these soils, except those of the humus soils, had been determined by four other workers under different sets of conditions. The values obtained by the other workers are not included in table 3, but they as well as the isohydric pH values are plotted in figure 2, which brings out clearly the wide variations that might be expected in pH measurements by the ordinary electrical method. The agreement between the isohydric pH values and the pH values determined by the antimony or quinhydrone electrode is better than that between the values determined by other workers. This better agreement might possibly be due to the fact that these three sets of values were determined in this laboratory on uniform samples under similar conditions whereas values determined by other workers were obtained on different samples, possibly under different sets of conditions. The necessity of specifying the conditions of such measurements is, therefore, quite obvious. It must be emphasized that the pH value of soil as determined by the electrical method is not a fundamental constant. The isohydric pH value, on the other hand, relates definitely to the state of saturation of the exchange complex and as such can define the soil much more satisfactorily than can the pH value determined by the usual methods in water suspension.

#### BUFFER CAPACITY OF SOILS

Buffer capacity of soils may be defined as the milliequivalents of alkali per 100 gm. of soil required to increase its pH value by 1 unit on the pH scale. Values for buffer capacity are included in table 3. If the buffer action of a soil be ascribed to clay, then it appears of interest to compare the buffer capacity of soils on the basis of clay, i.e., buffer capacity per 100 gm. of clay. These values included in table 3 are useful for comparing the types of clays in different soils.

#### pH VALUES OF HIGHLY ALKALINE SOILS

Highly alkaline soils form a class by themselves. They invariably contain a certain amount of sodium carbonate or bicarbonate, on account of which it is difficult to determine their isohydric pH value by the method outlined in this paper. They are, however, already in equilibrium with a sodium carbonate-bicarbonate buffer solution which determines their pH value. The reaction of such soils can be easily determined by finding the concentration of sodium carbonate-bicarbonate and then interpolating the pH value from the titration curve of NaOH with  $\text{CO}_2$ . The pH values of various mixtures of carbonate-bicarbonate at different concentrations were determined with the glass electrode, both in water and in 0.1 *N* KCl solution, the values in KCl solutions being uniformly lower by 0.2 pH than those in water. The following relation was found to hold between pH values and the carbonate-

bicarbonate ratio as well as the total concentration of the mixture in 0.1 *N* KCl solution:

$$\text{pH value} = 8.67 + 0.018 A - 0.0032 B$$

when

*B* = cc. of 0.1 *N* alkali (carbonate + bicarbonate) in 100 cc. solution  
*A* = per cent of  $\text{Na}_2\text{CO}_3$  in *B*.

From this relation the pH value of any alkali soil is determined by shaking the soil with 0.1 *N* KCl solution, filtering, and analyzing an aliquot of the filtrate for carbonate-bicarbonate. Since the pH value in KCl is lower than that in water solution by 0.2 pH, this amount is added to the pH value obtained from the formula to correspond to the pH value in water solution.

TABLE 4

*The pH values of alkali soils calculated from carbonate-bicarbonate ratio and determined directly (soil: water ratio 1:5)*

SOIL NO.	0.1 <i>N</i> CARBONATE	0.1 <i>N</i> BICARBONATE	pH CALCULATED (WATER SOLUTION)	pH FOUND (Sb ELECTRODE)
	cc.	cc.		
P.C. 57	0.6	0.7	9.70	9.8
P.C. 58	14.1	9.83	9.85	10.08
P.C. 59	0.0	1.0	8.87	8.66
P.C. 60	36.8	16.4	9.95	9.94

In table 4 are given pH values of certain typical alkali soils determined by the electrical method using the antimony electrode and the values obtained by titrating the 0.1 *N* KCl solution extract for carbonate-bicarbonate. The agreement is sufficiently close to illustrate the general principle involved. It might be pointed out that the method is not applicable unless the amount of sodium carbonate-bicarbonate in the soil is sufficiently large. For soils containing little or no free alkali carbonate-bicarbonate the usual isohydric method described in this paper is suitable.

#### SUMMARY

Isohydric pH value of a soil is defined as the pH value of a buffer solution which shows no change in reaction on coming into contact with the soil and which consequently brings about no change in the base content of the soil.

A method of determining isohydric pH value, titration curve, buffer capacity, and lime requirement of soils is described.

# MICROBIAL ACTIVITIES IN SOIL: IV. MICROFLORA OF DIFFERENT ZONAL SOIL TYPES DEVELOPED UNDER SIMILAR CLIMATIC CONDITIONS<sup>1</sup>

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In transitional areas between two different soil zones, it is not uncommon to find different zonal types of soil developed from the same parent material under similar climatic conditions. A forest type of soil may occur adjacent to a prairie type of soil, each possessing its own particular vegetative cover and inherent soil characteristics. The character of the humus formed from each specific type of vegetation under these conditions is generally believed to be chiefly responsible for the development of divergent soil properties. Organic materials and their mineralization may profoundly affect the physical, chemical, and biological properties of the soil, and consequently such factors as the formation, fertility, and erodibility of the soil. A thorough knowledge of the soil microflora and its activity, which are responsible for the mineralization of organic materials and the formation of humus, is, therefore, of fundamental importance.

The influence of different types of humus and of dissimilar soil characteristics on the nature and activity of the microflora in two zonal soil types similar in mechanical composition but developed under different climatic conditions was amply demonstrated in a previous publication (20). The chief purpose of the work presented in this paper was to ascertain the nature and seasonal activity of the microflora, in its natural environment, of two different zonal soil types developed from the same parent material under similar climatic conditions.

## EXPERIMENTAL PROCEDURE

Three virgin areas, two consisting of Palouse silt loam and the other of Helmer silt loam, were selected for this study. Both the Palouse and Helmer soils have developed on fine-textured loessial material under similar climatic conditions. The native vegetation on the Palouse soil is composed chiefly of tall bunch grass mixed with some bushy growth consisting of wild roses, snowberries, and buckbrush. A very thin irregular layer of litter composed largely of grass vegetation in various stages of decomposition covers the soil.

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The native vegetation of the Helmer soil is chiefly coniferous forest growth consisting of yellow, white, and lodgepole pine, fir, spruce, and cedar, although according to Agee et al. (1) some areas support white pine almost exclusively. A layer of coniferous duff ranging from 0.5 to 1.5 inches in thickness covers the soil and is not sharply demarcated from the mineral soil below, but merges gradually into it.

The mean annual temperature for the localities represented by these virgin areas is 47°F. The mean monthly minimum temperature, which occurs in January, is 22°, and the mean maximum monthly temperature, which occurs in July, is 82°. The extremes in temperature range from -20° in February to 104° in July. The mean annual precipitation for the virgin Palouse soil situated near Pullman, Washington, is 20.73 inches. The best figure available for the mean annual precipitation for the other two virgin areas represented by the Palouse and Helmer soils near Troy, Idaho, is 22.51 inches. This figure was obtained from the climatological data at Moscow, Idaho, which is situated 10 miles straight west of Troy and at approximately the same elevation. More than 60 per cent of the precipitation in these localities occurs during the winter months between November 1 and April 1. Snow lies on the ground intermittently for periods ranging from 2 to 6 weeks between December 1 and March 15. Very little precipitation occurs during the months of July, August, and September.

Weather conditions permitting, samples of soil were taken in the field at fairly regular intervals between February, 1935, and May, 1936, at depths of 0-0.5 inches, 0.5-4 inches, and 4-10 inches. The coarse rubbish on the surface of the soil was removed, and four auger borings obtained from as many permanently established centers scattered over an area of about 2 square rods were composited for each sample. The borings were made near the same local points at each sampling period. Plate counts were made for bacteria, actinomyces, and fungi in the samples taken at each depth; and for *Azotobacter*, aerobic cellulose-decomposing bacteria, and anaerobic nitrogen-fixing bacteria in composite samples of the three depths. The pH values and the redox potentials were determined on the air-dried samples taken at each depth.

The bacteria and actinomyces were grown on albuminate agar adjusted to pH 7.2, and the fungi, on potato dextrose agar adjusted to pH 3.5 by addition of sterilized 0.4 *N* citric acid. These media are described by Fred and Waksman (10, p. 9-18). The *Azotobacter*, aerobic cellulose-decomposing bacteria, and anaerobic nitrogen-fixing bacteria were determined by spreading suitable quantities of finely pulverized soil on silica gel plates. Winogradsky's (27) nutrient solutions were used for the growth of *Azotobacter* and anaerobic nitrogen-fixing bacteria, anaerobic conditions for the latter being produced with pyrogallol acid and potassium hydroxide. Waksman's (22) nutrient solution, together with filter paper, was used for the development of the aerobic cellulose-decomposing bacteria. All plates were incubated at 28°C.

The pH values and the redox potentials were determined by means of a glass

electrode apparatus, a suspension of 1 part of soil to 5 parts of distilled water being used for the pH determinations, and mixtures of 5 gm. of soil and 10 cc. of 0.1  $N$   $H_2SO_4$  according to the method of Peech and Batjer (16) being used for the redox potentials. The nitrogen was determined by the official Kjeldahl (3, p. 5-16) method, and the organic carbon in the soil and in the soil extracts, by the wet combustion method of Friedemann and Kendall (11).

#### EXPERIMENTAL RESULTS

##### *Seasonal variations in microbial activity*

Since moisture and temperature, as well as the food supply, affect biological activity fundamentally, numbers and activity of different kinds of microbes should follow, more or less closely, seasonal temperature and moisture changes in the soil. One should expect the largest numbers in late spring and early fall when temperature and moisture conditions are most nearly optimum, and the smallest numbers in winter and summer, because of low temperatures in winter and excessive dryness and high temperatures in summer. This assumption is not always borne out by facts. Snow (18), Cobb (6), Fehér (9), and Brown and Halversen (5) have presented evidence of extreme variability in the microbial population in the soil in different seasons. Waksman (21) found that microbial peaks vary with the type of soil and the depth, but he did not correlate these with the moisture content of the soil. Cutler, et al. (7) obtained maximum numbers in November, minimum numbers in February or March, and a secondary peak at the end of June. These did not correlate with seasonal changes in soil moisture, rainfall, or temperature. Erdman (8) found that the seasonal fluctuations in numbers in two years were not the same; although the maximum for both years was in June and the minimum in August, the count was low in February or March one year, and a second peak occurred in these same months the other year.

The data on numbers of bacteria, actinomyces, and fungi found in different seasons and at different depths in the Palouse and Helmer soils described in the foregoing section are presented in figures 1 to 3. They supply sufficient evidence for only a general statement regarding the effect of seasonal variations on numbers of soil microbes. Microbial peaks were manifested in the spring, especially during April, 1935, and in late fall and early winter during the months of October to January. With certain exceptions these peaks occurred at the same time at the different depths of the soil and were more or less of the same order for the different groups of microbes. The data in table 1 and figure 4 show that the moisture and temperature regimes were more nearly at optimum during the periods of maximum microbial numbers than during the intervals of minimum numbers. When temperatures became higher and the soil dryer, as in the month of July, or when temperatures dropped very low, as in the winter months, the numbers of microbes decreased. This decrease was generally less pronounced in the winter months when an ample supply of moisture was available than in the summer months when both high tempera-

tures and low moisture contents combined in inhibiting microbial activity. It may be noted also that the numbers of microbes in 1936 were not nearly so large as those at corresponding times in 1935, bearing out the observation of

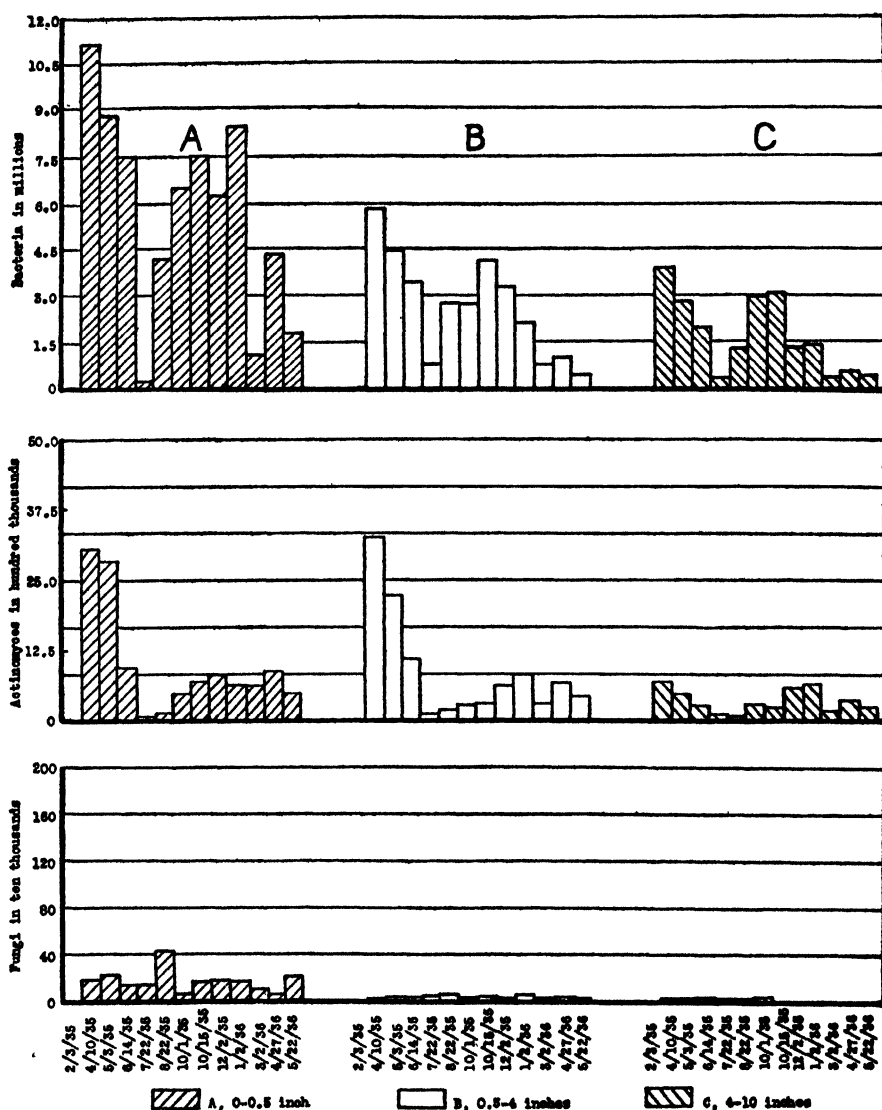


FIG. 1. NUMBERS OF BACTERIA, ACTINOMYCES, AND FUNGI PER GRAM OF DRY SOIL IN PALOUSE SILT LOAM (PULLMAN)

Erdman (8) that microbial peaks in two different years may vary. As indicated in table 1 and figure 4, the soil on the whole contained less moisture in 1936 during the months when samples were taken than at corresponding times

in 1935, and the temperatures in the early part of 1936 were somewhat lower than those at corresponding times in 1935. Both of these factors probably contributed to the differences in counts obtained.

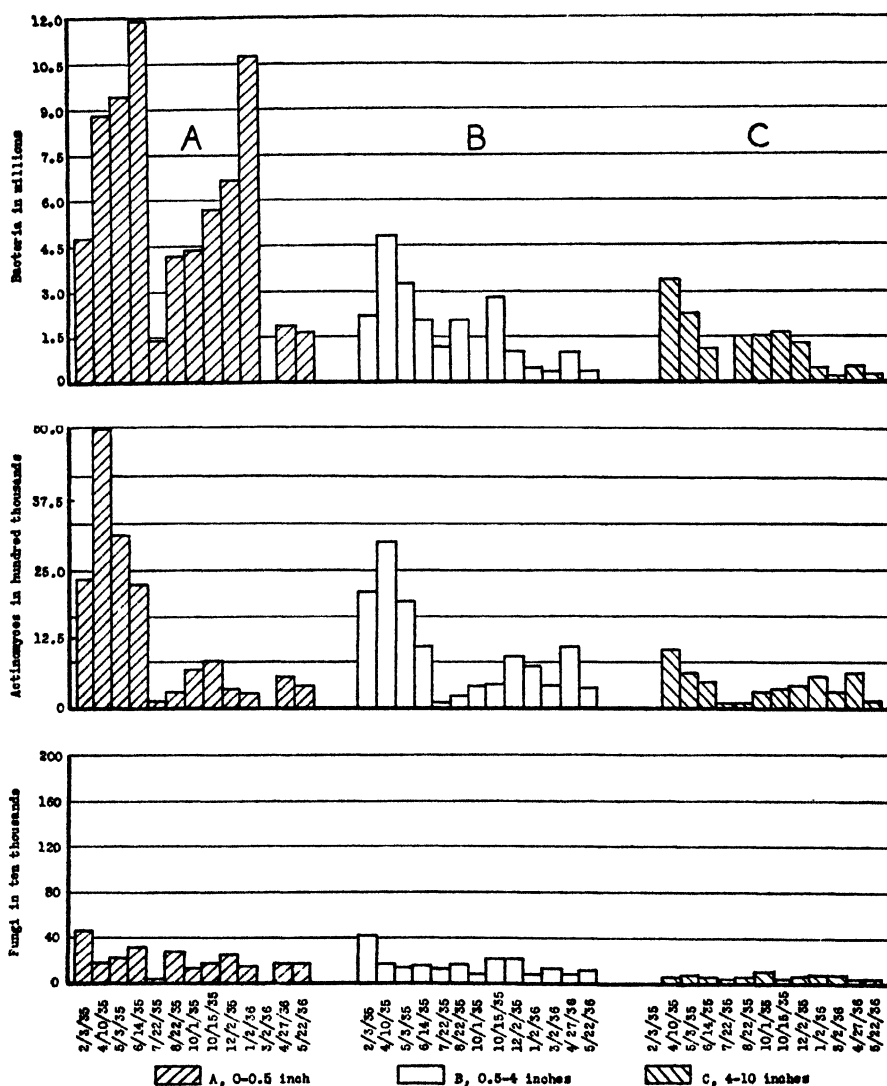


FIG. 2. NUMBERS OF BACTERIA, ACTINOMYCETES, AND FUNGI PER GRAM OF DRY SOIL IN PALOUSE SILT LOAM (TROY)

Although figures 1 to 3 indicate in a general way microbial maxima in spring and fall and minima in summer and late winter, corresponding broadly with the observations of Waksman and Starkey (24, p. 64-65) and of Cobb (6), these maxima and minima are by no means absolute. Within any particular



season, variations occurred which cannot be explained by the available moisture and temperature data. Errors arising from sampling and analysis may account in part for some of these variations, so that only the larger broader seasonal

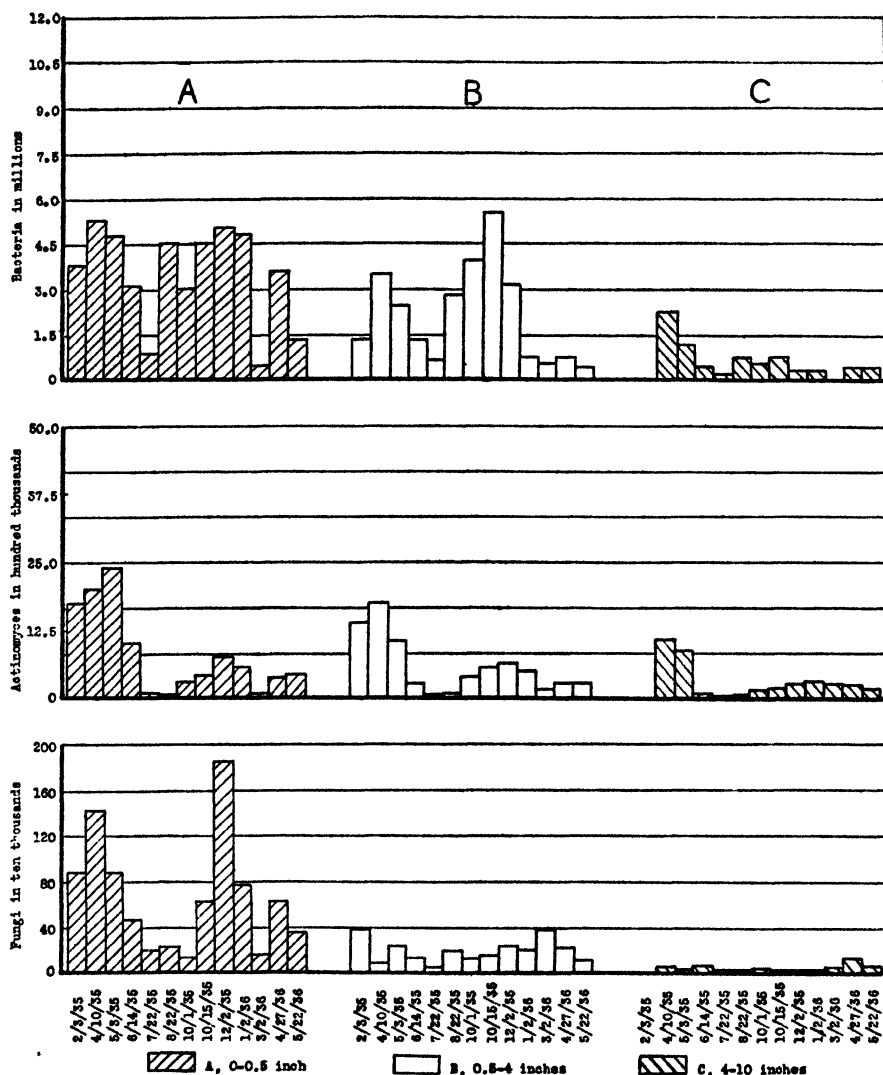


FIG. 3. NUMBERS OF BACTERIA, ACTINOMYCES, AND FUNGI PER GRAM OF DRY SOIL IN HELMER SILT LOAM

trends indicated by the microbial counts are consistent enough to warrant the mention they received.

The fact that numbers of microbes decrease with depth in the soil is commonly accepted and has been noted by Waksman (21), Cobb (6), and Snow

TABLE 1

*Climatological data for Moscow, Idaho, and for Pullman, Washington*

TIME	MEAN MONTHLY TEMPER- ATURE	MONTHLY MAXIMUM	MONTHLY MINIMUM	TOTAL PRECIPI- TATION	DATE OF SAM- PLING	MAXIMUM TEMPER- ATURE	MINIMUM TEMPER- ATURE	PRECIPI- TATION
	°F.	°F.	°F.	inches		°F.	°F.	inches

<i>Moscow, Idaho</i>								
1935:								
January . . . . .	30.6	52	-19	2.73				
February . . . . .	35.3	52	17	1.06	3	50	34	0
March . . . . .	35.8	64	9	2.55				
April . . . . .	43.7	65	21	2.93	10	60	31	0
May . . . . .	53.9	80	25	0.24	3	63	29	0
June . . . . .	58.8	85	35	0.61	14	68	45	0.27
July . . . . .	64.7	100	37	0.47	22	93	48	0
August . . . . .	63.6	99	30	0.34	22	89	48	0
September . . . . .	60.5	91	25	0.26				
October . . . . .	46.3	86	2	1.25	1	83	38	0
					15	53	35	0
November . . . . .	33.8	52	0	0.96				
December . . . . .	31.4	45	13	2.59	2	40	18	0
1936:								
January . . . . .	30.8	45	-2	5.12	2	41	32	0.83
February . . . . .	16.4	49	-20	2.17				
March . . . . .	36.6	61	16	1.92	2	56	35	0
April . . . . .	50.4	85	11	0.52	27	59	38	0
May . . . . .	58.0	91	34	0.86	22	65	42	0

<i>Pullman, Whitman County, Washington</i>								
1935:								
January . . . . .	31.2	52	-13	2.57				
February . . . . .	35.6	52	22	1.00				
March . . . . .	36.1	64	21	2.36				
April . . . . .	44.0	66	23	2.38	10	60	33	0
May . . . . .	53.8	78	33	0.33	3	65	33	0
June . . . . .	60.2	82	42	0.65	14	55	49	0.10
July . . . . .	66.7	98	42	0.32	22	91	54	0
August . . . . .	65.5	96	39	0.57	22	87	56	0
September . . . . .	62.6	88	33	0.26				
October . . . . .	47.4	82	4	0.95	1	80	50	0
					15	53	39	0
November . . . . .	33.6	52	4	0.76				
December . . . . .	31.2	45	16	1.96	2	29	22	0
1936:								
January . . . . .	31.3	45	5	4.29	2	41	34	0.05
February . . . . .	17.1	46	-13	1.87				
March . . . . .	37.0	62	17	1.85	2	59	36	0.02
April . . . . .	50.7	86	5.5	0.43	27	60	39	0.02
May . . . . .	59.3	91	37	1.17	22	66	45	0

(18), as well as by many other investigators. The data in figures 1 to 3 show this trend very distinctly with respect to the numbers of bacteria, actinomyces, and fungi even at the relatively shallow depths sampled. The bacteria and fungi decreased more rapidly in numbers with depth than did the actinomyces. As may be noted by comparing the soil moisture and the precipitation data in table 1 and figure 4, no consistent relationship existed between reduction in numbers of organisms with depth and changes in soil moisture content with depth, but there was a distinct correlation between the reduction in numbers of organisms with depth and the organic food supply, which was greatest at the surface and decreased sharply with depth. The difference in the amount and quality of air from the surface to the lower depth probably also contributed to the decrease in numbers with depth. The bacteria and fungi were more responsive to these factors than were the actinomyces, particularly in the surface 0.5-inch layer as compared with the 3.5-inch layer below it. On an average, the 0.5–4-inch layer yielded less than half as many bacteria and fungi, and



FIG. 4. PERCENTAGES OF SOIL MOISTURE BASED ON DRY WEIGHT AT DIFFERENT DEPTHS AND SAMPLING PERIODS

The moisture content of the surface 0–0.5-inch layers was not determined because of insufficient quantities of duff or litter.

about three-fourths as many actinomyces as the surface 0.5-inch layer. In the 4–10-inch layer the average numbers of bacteria and fungi ranged from 10 to 20 per cent, and those of the actinomyces from 30 to 35 per cent of the numbers in the respective groups in the 0.5-inch surface layers.

#### *Effect of climatic factors and vegetative cover on microbial activity*

Climatological data for Pullman, Washington, which are representative of the climatic conditions affecting the Palouse soil near Pullman, and those for Moscow, Idaho, which represent the climatic conditions affecting the Palouse and Helmer soils near Troy, are recorded in tables 1 and 2. The monthly precipitation; the monthly mean, maximum, and minimum temperatures; and the dates of sampling, as well as the precipitation and the maximum and minimum temperatures occurring on these dates, are presented in table 1. The figures on annual precipitation and mean annual temperatures for the years 1930 to 1935 inclusive are given in table 2.

The data on annual and monthly precipitation indicate a slightly more humid climate for the soils near Troy, Idaho, than for the Palouse soil near Pullman, Washington. Even this small difference in climatic conditions is reflected by the microbial activities in the two Palouse soils, as may be noted from the data in figures 1 to 3 with respect to total numbers of organisms and numbers of bacteria, actinomyces, and fungi separately for the three depths sampled. Although the total numbers and the percentages represented by each of the three groups of microbes fluctuated greatly at different times, the total numbers as well as the percentages of actinomyces and also of fungi in the two lower depths were greater, on the average, in the Palouse soil near Troy than in the Palouse soil near Pullman. The exception for the percentage of fungi in the surface layer of these two soils is due in part to low numbers of bacteria or to more than usual fluctuations in numbers of actinomyces and fungi at certain times.

TABLE 2

*Mean annual temperature and total annual precipitation for the years 1930 to 1935 inclusive*

YEAR	MOSCOW, IDAHO*		PULLMAN, WASHINGTON†	
	Temperature	Precipitation	Temperature	Precipitation
	°F.	inches	°F.	inches
1930	46.4	19.46	46.9	18.88
1931	47.7	21.01	47.7	20.27
1932	46.8	27.14	47.4	22.11
1933	47.5	29.63	48.3	26.62
1934	51.6	22.47	52.2	19.48
1935	46.4	15.99	47.3	14.11

\* Elevation 2,628 feet.

† Elevation, 2550 feet.

The effect of the difference in vegetative cover of the Palouse and Helmer soils is clearly expressed by the types of microflora and the numbers of organisms in the various groups. As may be noted by comparing the data in figures 2 and 3, the bacteria, although relatively plentiful, were less numerous and the fungi much more numerous in the 0.5-inch layer and also to some extent in the 0.5-4-inch layer of the Helmer soil than those at the same depths in the Palouse soil. The actinomyces were more numerous at all depths in the latter soil, although the differences between the two soils in percentages of actinomyces on the basis of total microbial population are not very significant. The higher numbers of fungi in the Helmer soil, which bears coniferous trees, as compared with those in the two Palouse soils, which are covered with grass vegetation, is in accord with established conceptions. The comparatively large numbers of bacteria and actinomyces in the Helmer soil are not unusual. Many investigators, including Waksman et al. (25), Powers and Bollen (17), Aquino (2), and Greene (13), obtained similar results.

Large numbers of aerobic cellulose-decomposing bacteria have been found in many soils by various investigators. Anaerobic nitrogen-fixing bacteria also have been observed to be relatively numerous in certain soils. Willis (26) and Bokor (4) found rather large numbers in acid soils. These two groups of organisms, therefore, may play an important part in the biological processes in certain soils. The numbers of aerobic cellulose-decomposing bacteria and

TABLE 3  
*Aerobic cellulose-decomposing bacteria per gram of soil in the surface 10 inches*

DATE OF SAMPLING	HELMER SOIL	PALOUSE SOIL (TROY)	PALOUSE SOIL (PULLMAN)
2/ 3/35	0	20	
4/10/35	0	0	5
5/ 3/35		37	150
6/14/35	45	50	60
7/22/35	0	115	67
8/22/35	112	75	150
10/ 1/35	12	62	45
10/15/35	35	22	50
12/ 2/35	2	70	70
1/ 2/36	50	210	230
3/ 2/36	7	5	12
4/27/36	146	246	120
5/22/36	23	63	53

TABLE 4  
*Anaerobic nitrogen-fixing bacteria per gram of soil in the surface 10 inches*

DATE OF SAMPLING	HELMER SOIL	PALOUSE SOIL (TROY)	PALOUSE SOIL (PULLMAN)
2/ 3/35	0	0	
4/10/35	50	100	250
5/ 3/35	5	20	17
6/14/35	35	30	150
7/22/35	27	40	137
8/22/35	25	80	75
10/ 1/35	25	17	67
10/15/35	100	40	50
12/ 2/35	25	65	12
1/ 2/36	5	0	45
3/ 2/36	10	40	145

anaerobic nitrogen-fixing bacteria which were determined on composite samples of the three depths in each of the three soils investigated are recorded in tables 3 and 4, in which it is shown that these organisms were never very active. Their numbers fluctuated too greatly to warrant any conclusion with respect to seasonal trends or effect of climate and vegetation. The Palouse soil near Pullman had a somewhat larger population of anaerobic nitrogen fixers than did the other two soils, but the difference was not significant.

No *Azotobacter* were found at any time in any of the three soils, which ranged in pH values from 5.44 to 6.53 for the Helmer soil and from 6.18 to 7.13 for the Palouse soils, the variations depending on the depth in the soil and the season. In a study of the *Azotobacter* population in a number of Helmer soils which varied in pH value from 5.66 to 7.2, Gibbs and Batchelor (12) found these organisms in 24 per cent of the soils. As reported in a previous publication (19) these organisms were present also in certain soils with a pH value of 5.5 or less and in cultivated Palouse silt loam located near the area of virgin Palouse soil at Pullman. Soil reaction alone does not explain the absence of *Azotobacter* in the Palouse and Helmer soils. Since the publication of the aforementioned study of *Azotobacter*, which also reports the presence of maximum

TABLE 5  
*pH and Eh values of the various soils at different times during the year*

DATE OF SAMPLING	HELMER SOIL			PALOUSE SOIL (TROY)			PALOUSE SOIL (PULLMAN)		
	0-0.5 inches	0.5-4 inches	4-10 inches	0-0.5 inches	0.5-4 inches	4-10 inches	0-0.5 inches	0.5-4 inches	4-10 inches
<i>pH Values</i>									
5/ 3/35	6.53	6.53	6.16	6.53	6.46	6.32	6.78	6.83	6.70
7/22/35	5.90	6.15	6.00	6.30	6.40	6.40	6.51	6.93	6.93
10/ 1/35	5.82	6.06	6.25	6.49	6.30	6.26	6.98	6.76	6.70
4/27/36	6.28	6.21	6.15	6.18	6.43	6.28	6.76	6.74	6.55
<i>Eh Values*</i>									
5/ 3/35	754.8	821.0	808.0	711.2	808.8	836.0	715.4	786.0	798.0
7/22/35	633.4	763.0	731.0	608.8	788.8	801.8	605.4	756.4	778.4
10/ 1/35	627.5	816.0	845.5	620.1	798.0	927.8	617.9	783.8	803.0
4/27/36	622.0	774.5	794.6	616.5		782.7	609.0	767.4	800.4

\* The Eh values are the oxidation-reduction potentials calculated to a standard pH value of 2, using the correction factor of 80 millivolts per change of 1 pH unit, according to Peech and Batjer (16).

numbers of these organisms in Palouse silt loam in late fall and early spring and very few or none in the summer months, unpublished results of periodical determinations of *Azotobacter* in this soil show that for no accountable reason these organisms have disappeared completely. This condition applied to both the virgin and the cultivated Palouse soils and apparently also to the virgin Helmer soils. Reaction is not the limiting factor, and no data are as yet available which may explain the absence or disappearance of the *Azotobacter* from these soils.

*Soil reaction, redox potentials, and humus content in relation to microbial activity*

The pH and Eh values of the samples of the Helmer and the two Palouse soils taken at the three depths were determined at each sampling. Because of

the relatively small differences in values obtained during different times of the year, only the results of a few typical determinations are given in table 5.

Forest soils, particularly near the surface, are reputed to be more acid than grassland soils, partly because of greater humidity but particularly because of the peculiar nature of the organic residues. The nature of the organic residues returned to the Helmer soil probably is chiefly responsible for the lower pH values of this soil as compared with those of the Palouse soil in the same locality. Probably the fungus population, which was larger in the Helmer soil than in the Palouse soils, was favored also by the more acid reaction. The slightly lower pH values indicated for the Palouse soil near Troy than for the one near Pullman probably is due to a slightly more humid climate in the Troy area. This, rather than the difference in soil reaction, probably accounts for the more active microbial development noted in the Palouse soil near Troy. Cobb (6) lists a number of investigators who found that small changes in soil reaction have no apparent relationship to the numbers of microbes present in the soil although different types of microbes may be strongly influenced by reaction. The data in table 5 indicate no apparent relationship between depth in the soil and reaction or seasonal variations in pH values.

The method of Peech and Batjer (16), slightly modified, was used for the determination of the redox potentials of the soils in this investigation. Instead of keeping the soil-acid mixture standing for 24 hours with intermittent shaking, as suggested by Peech and Batjer, we reduced the time factor to 8 hours and allowed the soil-acid mixture to stand in contact with the electrode for 20 minutes before making the readings. A platinum electrode was used for the determinations of the redox potentials, and a glass electrode for the pH values. Preliminary trials with different soils resulted in a satisfactory equilibrium of the system by this procedure. The Eh values recorded in table 5 were obtained by this procedure and represent the oxidation-reduction potentials calculated to a standard pH value of 2.

The most significant differences in the Eh values are those between the 0-0.5-inch layers and the two layers below them. In every case the Eh value of the surface, highly organic layer was definitely lower than the Eh values the two underlying layers. The differences in the values of the other two layers of the various soils and in different seasons are not significant. No correlation could be established between the differences in redox potentials and the differences in microbial activity in the various soils.

Heintze (14) states that under normal conditions the factors responsible for oxidation-reduction equilibria are the reserves of oxidized and reduced materials rather than the temporary occurrence of highly active substances. From numerous waterlogging experiments he found marked decreases in Eh values for soils known to contain organic matter capable of rapid decomposition, as soon as soil moisture content and reaction become favorable. Both the Helmer and Palouse soils contain organic materials which are susceptible to rapid decomposition under favorable conditions, as will be pointed out in the

following paper in this series. It is not presumptuous, therefore, to suppose that in the highly organic surface layer of these two soils are present reducing organic compounds which are responsible for the observed low Eh values.

Data on Melbourne and Palouse soils reported in the preceding paper of this series (20) indicate that although the Melbourne soil, which bears forest vegetation, contains much more humus than the Palouse soil, which bears grass vegetation, the latter had the larger microbial population and by far the smaller number of fungi. A similar microbial relationship was manifested under field conditions in the Palouse and Helmer soils near Troy. As may be noted from the data in table 6, the humus and the surface residue of the Palouse soil contain larger amounts of combined water-soluble and  $H_2SO_4$ -soluble carbon, and less  $H_2SO_4$ -insoluble carbon than did the same substances of the Helmer soil. Evidently the nature of the humus rather than the amount within certain limits is the more influential in determining the type and numbers of microbes. The fact that organic residues and humus derived from forest

TABLE 6

*Organic carbon and nitrogen contents of the organic residue layer and of the surface 10 inches of the Palouse and Helmer soils near Troy, Idaho*

SOIL	ORGANIC C	TOTAL N	C/N	FRACTIONS IN PER CENT OF TOTAL CARBON		
				Water- soluble C	$H_2SO_4$ - soluble C	$H_2SO_4$ - insoluble C
	<i>per cent</i>	<i>per cent</i>				
Palouse soil . . . . .	3.46	0.2091	16.5	3.38	28.01	65.43
Palouse soil litter . . . . .	32.64	0.7035	46.4	5.40	51.73	37.56
Helmer soil . . . . .	2.32	0.1001	23.2	3.19	26.44	69.88
Helmer soil duff . . . . .	36.69	0.5782	63.5	6.92	27.03	62.08

vegetation were found to be favorable for fungal growth is in accord with established conceptions as mentioned previously.

The marked difference in humus content of the Palouse and Helmer soils, which have developed from identical parent materials and under practically identical climatic conditions, slopes, and exposures, is noteworthy. One would expect at least as much annual production of vegetative growth from forest vegetation as from grass vegetation under such conditions, because loss of moisture by evaporation is less under forest cover than that under grass cover, and tree roots are capable of obtaining water from lower depths than those accessible to grass roots, provided the subsoil is permeable to roots, as is the case in these two soils. Virtually all the vegetative growth including roots and top growth is eventually returned to the soil under virgin conditions. The Helmer soil, as pointed out previously, has a duff cover ranging from 0.5 to 1.5 inches in thickness, whereas the Palouse soil has only a very thin layer of litter covering the surface irregularly. This indicates that the organic residue



of the top growth on the forest soil has a tendency to accumulate and that of the top growth on the grassland soil is decomposing as rapidly as it is being formed. Evidently not all the humus in the soil is derived from the top growth of the vegetative cover. Pedologists, in general, believe that the plant roots, especially in grassland soils, play a more important part in soil organic matter relationships than has hitherto been recognized.

Information in the literature regarding the quantities of organic residues added annually to the surface of soils by different kinds of native vegetation

TABLE 7

*Grass vegetation on the Palouse soil and root distribution in the Palouse and Helmer soils*

SAMPLING AREA	SURFACE GROWTH		ROOT DISTRIBUTION			
	Oven-dry weight per square yard		Oven-dry weight per square foot			
	Palouse soil	Helmer soil	Palouse soil		Helmer soil	
			0-4 inches	4-10 inches	0-4 inches	4-10 inches
	gm.		gm.	gm.	gm.	gm.
1	143.5		202.5	53.5	41.6	86.0
2	147.5		110.5	32.7	25.8	21.5
3	120.9		100.0	73.0	42.3	40.0
4	109.9		101.0	27.5	71.9	62.5
5	145.7		24.5	16.5	57.4	38.0
Total.....	667.5		538.5	203.2	239.0	248.0
Average.....	133.5		107.7	40.6	47.8	49.6
Equivalent in tons per acre.....	0.711	1.37*	5.16	1.95	2.29	2.38
Character of the root material			Mostly fine matty, tough roots, mixed with some larger herbaceous and shrub roots. Uniformly distributed in both layers.		Some small, fine roots, but major part of the weight due to larger tree and shrub roots. Irregularly distributed in both layers.	

\* Based on averages of the data given by Waksman (23, p. 221-226).

is not extensive, and that with respect to the amount of root material present at different depths in forest and grassland soils is scarce indeed. Waksman (23, p. 221-226) refers to a number of investigators whose results show an average of about 2,500 or 3,000 pounds an acre of tree residues added annually to the surface of forest soils. It was not convenient to determine the amount of tree residues annually returned to the Helmer soil, but judged from the nature of the forest growth on this soil, the amount probably would come close to average figures. An attempt was made to determine the amount of top growth produced annually on the Palouse soil and also of the root distribution

at the depths of 0 to 4 inches and 4 to 10 inches in both the Palouse and the Helmer soils. Five sampling areas bearing typical vegetative covers of grass and forest growth respectively were selected. The size of sampling spots for the grass vegetation on the Palouse soil was 1 square yard, and that for the root distribution in both the Palouse and the Helmer soils was 1 square foot. The grass vegetation was cut close to the ground and oven dried. The root materials were obtained by removing blocks of soil 1 square foot in size at the required depths. The roots were washed free from soil and oven dried. The results of these determinations are recorded in table 7.

Because of natural irregularities in the distribution of native plants, a considerable variation in the weight of root materials in different sampling spots was obtained, but the averages should be fairly representative of field conditions. On the basis of the average figures in table 7, it appears that the amount of top growth annually returned to the Helmer soil should be nearly twice the amount returned to the Palouse soil, but the Palouse soil should contain considerably more root material in the surface 10-inch layer than the Helmer soil. The total quantity of organic materials including top growth and roots available for these two soils at a depth of 10 inches, the depth sampled for organic carbon determinations, although apparently greater for the Palouse than for the Helmer soil may not be sufficient, however, to account for the fact the humus content of the Helmer soil is only about two-thirds as large as that of the Palouse soil.

The nature of the root system in contributing to the humus supply is a factor worthy of consideration. The fine, uniform root system of the Palouse soil may favor more rapid decomposition than the larger, coarser roots in the Helmer soil. More important than the nature of the root system in the formation of humus is the composition and particularly the nitrogen content of the organic materials from which humus is formed. The fact that the nitrogen content of both the humus and the surface organic residue of the Helmer soil is considerably lower than that of comparable substances in the Palouse soil has already been mentioned. In a recent publication from this laboratory (15) it was pointed out that the formation of humus from plant residues added to Palouse silt loam is directly influenced by the nitrogen content of the residues and the amount of available nitrogen present in the soil. The evidence presented there offers convincing proof that the humus formed in the soil has a definite carbon-nitrogen ratio regardless of the quantity of carbonaceous material that is available for decomposition. More carbon was shown to be dissipated by  $\text{CO}_2$  evolution in the transformation of low-nitrogen plant residues than that in the transformation of high-nitrogen plant residues, such as alfalfa hay, or of low-nitrogen plant residues supplemented with available nitrogen. Although the more suitable moisture regime for microbial activity, the lower root content, and the larger fungus population of the Helmer soil may be contributory to the lower humus content of this soil as compared with the Palouse soil, it is not unlikely that one of the principal reasons for this difference

is the comparatively low nitrogen content of the coniferous tree residues from which the humus in the Helmer soil is derived, rather than the difference in the total amounts of plant residues annually returned to these two soils. This point, however, remains to be verified by further investigation.

#### SUMMARY

Microbial analyses were made at various times of the year at depths of 0 to 0.5, 0.5 to 4, and 4 to 10 inches in one area of virgin Helmer silt loam and in two areas of virgin Palouse silt loam developed from identical parent materials under similar climatic conditions. The pH values, oxidation-reduction potentials, and moisture contents of the soil samples obtained at the various times were also determined.

A decided variation in total numbers of microbes occurred during different seasons. Microbial peaks were obtained in spring, especially in April, and in late fall and early winter. Minima occurred in July and August and also in February. The same trend was manifested at the different depths sampled.

The numbers of microbes decreased sharply with depth. On the average, the microbial population in the surface 0.5 inch layers was from three to four times as large as that in the 4-10-inch layers. The three soils yielded similar results in this respect.

The Helmer soil supported the smallest total microbial population, the smallest number of bacteria, and the largest number of fungi. The total microbial population in the two Palouse soils did not vary greatly, but the Palouse soil at Troy, Idaho, contained somewhat larger numbers of actinomyces and fungi, particularly in the two lower depths, than did the Palouse soil at Pullman, Washington. The actinomyces population was much larger than the fungus population and did not vary greatly in the three soils.

The aerobic cellulose-decomposing bacteria and anaerobic nitrogen-fixing bacteria in these soils were relatively few in numbers and fluctuated so much at various times that no significant trend with respect to effects of season or native vegetation was indicated. The *Azotobacter* species was not present in any of the soils at any time.

The pH values of the Helmer soil were lower than those of the Palouse soil in the same locality, probably because of the peculiar nature of the organic residue returned to the soil. The pH values of the Palouse soil at Troy were slightly lower than those of the Palouse soil at Pullman, probably on account of the more humid climate in the Troy area.

The oxidation-reduction potentials were lower in the surface 0.5-inch layer of the three soils than in the two underlying layers. No consistent difference in the oxidation-reduction potential values of the three soils was obtained, and no correlation was apparent between these values and the differences in microbial activity in the various soils.

The observed differences in total microbial population and numbers in specific groups of microbes are assumed to be the result of differences in mois-

ture, reaction, and especially the nature of the organic food supply. Both the humus and the surface organic residue of the Helmer soil had less nitrogen, wider carbon-nitrogen ratios, and more  $H_2SO_4$  insoluble carbon than did the comparable materials of the Palouse soils.

Determinations of the top growth of grass vegetation on the Palouse soil indicated that the amount of dry matter produced by this vegetation and consequently returned to the surface of the soil is about 0.7 tons per acre annually. This, according to available data, is about half as much dry matter as is annually returned to forest soils by the average top growth of forest vegetation. The average weights of oven-dried root material in the surface 10-inch layer were approximately 7 tons and 4.7 tons an acre for the Palouse and Helmer soils respectively.

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## BOOK REVIEWS

*Studies on Wheat Grown Under Constant Conditions.* By H. L. VAN DE SANDE-BAKHUYZEN. Food Research Institute, Stanford University, California, 1937. Pp. xvi + 400, tables 57, figs. 27. Price \$4.00.

This volume represents another addition to the series of contributions that have come from the Food Research Institute. These contributions have broadened our outlook on the present and potential food resources of the world.

In undertaking the work dealt with in this treatise, the authors set themselves a clearly defined task. As is noted in the directors' preface:

This book is a contribution in a field hitherto but little cultivated—the physiology of plants grown under constant conditions. The investigations upon which it is based were undertaken in connection with early studies at the Food Research Institute upon the forecasting of crop yields from the weather, in which it became clear that some of the correlations between the weather at various stages of a crop's growth and the size of the crop could not be explained on the basis of existing knowledge regarding the physiology of growth.

The contents of the book are divided into seven parts, entitled, respectively: The Growth Curve in Annual Plants; Methods and Materials; General Growth Features; Dry Weight and Moisture Content of the Different Organs; Dry Weight and Moisture of the Standard Plant; Nitrogen and Carbon of the Organs; and Nitrogen Metabolism in Relation to Growth and Development. A bibliography and an index are also included in the book.

The physiologist and the agronomist will find much in this book that will fill gaps in the earlier information about the growth of wheat and, in a sense, about the growth of plants in general. Economists, as well as plant physiologists, will gain a clear conception of the limiting factors in the production of our cereal crops.

*Catalysis.* By GEORG-MARIA SCHWAB. Translated by Hugh S. Taylor and R. Spence. D. Van Nostrand Company, Inc., New York, 1937. Pp. xi + 357, tables 38, figs. 38. Price \$4.25.

The translator—Hugh S. Taylor—notes that

Developments in the field of catalytic reactions by no means suffered to the same extent as conditions in the economic world. When the time came to issue the volume in English it was found necessary to supplement the original text by copious additions from the recent literature. These were supplied both by the author and the translators.

The author's purpose in writing the book is indicated in the preface. Here the author says:

The significance of catalysis in the field of chemistry is being brought more and more to our attention, encouraged by the development of technology on the one hand and of scientific

biology on the other. The perfection of the indispensable physiochemical foundations of the catalysis has, in general, kept pace with the consequent increasing necessity for a scientific treatment of the subject, and chemical kinetics particularly, in its present state of rapidly advancing development, affords a generously proportioned substructure. It is true that new, as yet unsolved, and more deeply penetrating problems are now emerging in growing numbers from behind older questions which have been cleared up, but it is precisely for this reason that an attempt at a comprehensive consideration of catalysis from the standpoint of chemical kinetics promises some reward.

The book is made up of 19 chapters, accompanied by an author index and a subject index. The topics dealt with in the several chapters are as follows: Historical Introduction; General Introduction; Catalysis of Homogeneous Gas Reactions, I. Simple Reactions; Catalysis of Homogeneous Gas Reactions, II. Chain Reactions; Homogeneous Catalysis in Solution, I. The Concept of Intermediate Steps; Homogeneous Catalysis in Solution, II. Fundamentals of Ion Catalysis; Homogeneous Catalysis in Solution, III. The Catalytic Salt Effect; Homogeneous Catalysis in Solution, IV. The Influence of Solvent; Negative Catalysis in Solution; Heterogeneous Catalysis. General Introduction; Adsorption; Kinetics of Heterogeneous Catalysis; Activation and the Mechanisms of Catalysis; Selective Catalysis and Poisons; The State of a Catalyst; Mixed Catalysts, Supported Catalysts and Promoter Action; Heterogeneous Chain Reactions; Catalysis in Solid Systems; and Micro-Heterogeneous and Bio-Catalysts.

*Catalysis* will be enthusiastically received by many workers in the specialized field of chemistry. The facts and interpretations presented by the author should be particularly helpful to the biochemist. The book should find wide application and should prove serviceable to the student and teacher.

*Statistical Methods.* By GEORGE W. SNEDECOR. Collegiate Press, Inc., Ames, Iowa, 1937. Pp. xiii + 341, tables 133, figs. 22. Price \$3.75.

The present work is one of the interesting projects of the Collegiate Press, Inc., at Ames, Iowa. It serves to remind one of the rapid strides made by abstract and applied science in the midwestern and northwestern states. The rule of thumb methods of the pioneers have been replaced in large measure by the more exact methods of the investigator and statistician. To quote the author:

Like all other sciences, statistics is in a stage of rapid evolution. During the last 20 years new discoveries have swiftly succeeded each other, fruitful syntheses have been effected, novel modes of thought have developed and a whole series of brand new statistical methods have been marketed. The biologist who has not been able to keep abreast of the progress of statistics finds himself a bit confused by the new ideas and technical terms. It is thought that he will welcome a statement of them in a form that will not require too much distraction of his attention from necessary professional duties.

Aside from the introduction, the book is made up of 16 chapters, a general index, and an index of symbols. The chapters are named, respectively: Experiments on Attributes; An Experiment Designed to Compare Measure-

ments of Individuals; Sampling from a Normally Distributed Population; An Experiment Designed to Compare Two Groups; Short Cuts and Approximations; Linear Regression; Correlation; Large Sample Theory; Enumeration Data with Multiple Degrees of Freedom; Experiments Involving More than Two Groups of Measurement Data. Analysis of Variance; Analysis of Variance with Two Criteria of Classification; Two Variates in Two or More Groups. Covariance; Multiple Regression and Covariance; Curvilinear Regression; Individual Degrees of Freedom; and Labor Samples of Enumeration Data. Binomial and Poisson Distributions.

In these days of local and national planning, the statistical methods discussed by the author should prove very helpful in connection with studies related to biological and other trends. Certainly, our tools are now more perfect for measuring various probabilities. The present work should find a place on the reference shelf of the teacher and investigator.

*Biological Laboratory Technique.* By J. BRONTË GATENBY. Chemical Publishing Co. of N. Y., Inc., New York, 1937. Pp. vii + 130, ill. 8. Price \$3.00.

The author tells us in the preface that "This book has been written in a practical manner for two classes of persons, first the University teacher or student who may desire a short and simple introduction to the most recent and established practice in microtomy, and secondly, the amateur who may wish to make a small laboratory of his own, and is unaware that a good part of modern laboratory research is carried out with the simplest apparatus."

The book is made up of nine chapters, designated as follows: Introduction. Laboratory Apparatus; Treatment of Living Cells, Saline Media, Vital Staining; Fixed and Stained Smears; Microchemical Tests in Smears; Whole Mounts; Fixation Methods; Paraffin, Dioxan and N-Butyl Alcohol and Celloidin Imbedding; Stains and Staining; and Notes for Histology and Embryology Students, and Addenda.

Despite the fact that other laboratory manuals relating to biological technique are available, the present work has much to be said for it from the point of view of the arrangement of the subject matter, the clearness and conciseness of statement, and the reference to the more recent contributions to biological laboratory technique.

*Economics of Agriculture.* By A. P. VAN DER POST. Central News Agency, Limited, Johannesburg, South Africa, 1937. Pp. xxvii + 663, tables 67, figs. 20.

Interest in agricultural economics is being stimulated by important political and social trends. Here and there, economic and fiscal policies have undergone far-reaching changes—partly because of the growth of economic nationalisms. Imports and exports of agricultural products have been modified in response to political pressure, new political and party alignments, and the emphasis now



being laid on economic self-sufficiency. The author is well aware of these facts, for he notes in his preface:

The difficulties which agriculture has experienced since the Great War have caused attention more and more to be focused on the problems of that great industry. The economic aspect of these problems, however, is but imperfectly understood and the attention bestowed on them has consequently in many respects been misdirected, solutions being sought in uneconomic rather than economic action. Moreover in the treatment of economics, on the one hand, and of agriculture, on the other hand, the fundamental interdependence of all economic activity and, therefore, of all forms of human endeavor and industry is all too often ignored. The result is neglect of agriculture in the treatment of economics and *per contra* of economics in the treatment of agriculture and, if so far as practical policy is concerned, failure to consider the possible effect of measures taken in one sphere on other spheres of economical endeavor.

The nature of the material dealt with by the author is clearly shown by the titles of the 22 chapters of which the book is made up. The several chapters are designated, respectively: Introduction: Agriculture, Economics, Agricultural Economics and Farm Management; The Origin, Rise and Development of Agriculture; The Factors of Production; The Combination of the Factors of Production in Agriculture; The Personal Factor in Agricultural Production; Capital as a Factor of Agricultural Production; Land as a Factor of Agricultural Production (a) Character; Land as a Factor of Agricultural Production (b) Size of Holding; Agricultural Regions, Systems and Practices; The Economic Basis of Rural Development (a) General Economic Policy: the Trek to Town; The Economic Basis of Rural Development (b) Principles to be observed in Land Settlement; The Economic Basis of Rural Development (c) Irrigation Settlements; The Distribution of the Agricultural Income; The Marketing of Agricultural Produce (a) Value, Demand and Supply, Money, Price; The Marketing of Agricultural Produce (b) Meaning of Marketing, Methods, Middlemen, Marketing Costs; The Marketing of Agricultural Produce (c) Co-operation and Sale through One Channel; International Trade (a) Origin and Nature, Foreign Exchange, Advantages and Disadvantages, Importance to Agriculture; International Trade (b) Import Duties, Protection, Free Trade and Agriculture; Trade Cycles and Agriculture; Farm Relief; Agricultural Credit; Some Economic Aspects of the Agriculture of the Union of South Africa.

It is obvious that the author has drawn extensively on information from various sources. He makes his acknowledgments to material of American, Australian, Dutch, English, French, German, South African, South American, and New Zealand origin. Because of the wide range of his studies and interpretations, his deductions are all the more interesting. The reader will find in the book much that is enlightening and entertaining as well.

*Crop Management and Soil Conservation.* By JOSEPH F. COX AND LYMAN E. JACKSON. John Wiley & Sons, Inc., New York, 1937. Pp. xvii + 610, tables 36, figs. 199.

The wide publicity now being given to conservation, in general, and to soil conservation, in particular, has made many persons conservation-conscious. As a nation, we may be fairly charged with sins of omission as well as of commission in dealing with our land resources. Much of the soil organic matter has been dissipated. Sheet erosion and gully erosion have depreciated the value of many millions of acres, and the plant-food resources of our soils have been diminished to a point where in many areas crop production is no longer profitable. The federal government and the states are now trying to repair some of the damage that has been done and to restore the fertility of the land wherever this may be practicable. Hence, *Crop Management and Soil Conservation* is a particularly timely contribution on the subject.

The following statement in the preface, made by the editors and authors, is indicative of their interpretation of their task:

It is the primary object of this book in dealing with specific crops to present in a simple way the major operations that will enable the grower to grow and market his crops successfully. Practices that are effective in reducing the cost of production, improving crop qualities, maintaining fertility, and marketing efficiently are given particular emphasis. The solid and lasting achievements of recent years in developing a national program directed toward the balancing of crop production and the conservation of soils are given an important place in this book.

The book is divided into two parts containing, altogether, 34 chapters, an appendix, and an index. The several chapters are entitled: Balancing Crop Production and Maintaining Fertility; Surveying Crop Production from the Farm Management Standpoint; The Nature and Use of Crop Plants; The Growth and Maturing of Crop Plants; The Nature of Soils; Protecting our Soil from Erosion; Manuring, Fertilizing, and Liming Field Crops; Growing Best-Adapted Crops; Securing the Best Crop Varieties; Growing Seed on the Farm; Growing Crops in Rotation; Preparing Seed Beds, Planting and Cultivating Crops; Harvesting and Storing Crops; Marketing Crops and Federal Programs for Agriculture; Controlling Crop Diseases; Controlling Insect Pests; Controlling Weeds; Planning Improvements in Crop Management and Soil Conservation Programs for Specific Farms; Corn Growing; Wheat and Rye Growing; Oats, Barley, Buckwheat and Flax Growing; Sorghum Growing; Growing Soybeans and Cowpeas; Growing the Clovers; Alfalfa and Sweet Clover Growing; Growing Lespedeza and Other Legumes; Growing Grasses for Hay and Pasture; Managing Pastures; Growing Annual Grasses and Legumes for Hay, Pasture, Green Manuring, and Cover-Crop Purposes; Potato Growing; Field-Bean Growing; Sugar-Beet Growing and the Growing of Other Root Crops; Growing Special Field-Truck Crops; and Growing Home Food and Feed Crops.

This book will be particularly useful to teachers of vocational agriculture. It should prove to be of value also to the general reader, the progressive farmer, and to teachers in our agricultural colleges.

*Potash Deficiency Symptoms.* By OSKAR ECKSTEIN, ALBERT BRUNO, AND J. W. TURRENTINE. Verlagsgesellschaft für Ackerbau M. B. H., Berlin, 1937. Pp. xii + 235, ill. 54.

For many years the technologist has been trying to define the symptoms related to definite deficiencies in plants. Much progress has been made in this field in recent years. The scientific definitions have reached a point where the landowner may take advantage of the information that has been made available to the end that he might learn from the crop itself what may be lacking in the soil. The present volume is a valuable contribution on the subject of plant deficiency symptoms with particular reference to potash.

In the foreword, written by the noted plant physiologist Gabriel Bertrand, the following is noted:

On passing from the realms of theory to the practical consideration of the problem, in other words from the laboratory to the field, complications arise. The soil is an exceedingly complex structure the nature of which is ill defined. It not only contains mineral substances of varying composition and properties but is also populated by innumerable animal and vegetable micro-organisms, which compete with the crop for the available supply of potash. On the other hand climatic factors beyond man's control such as light, heat, and above all dew, mist and rain, influence the yields to a considerable extent and tend sometimes to mask the effect of the fertilizers applied. It is, however, very difficult for agriculturists to ascertain whether their soils contain a sufficient supply of available "potash," and it is to assist them in solving this important problem that Messrs. Eckstein, Bruno and Turrentine have published this volume which I have great pleasure in sponsoring.

The first part of the book contains a discussion of the general symptoms of potash deficiency. The second part deals with potash deficiency symptoms of various cultivated crops. The deficiency symptoms as manifested by the different parts of the plant are fully discussed. A discussion is also included on the secondary effect of potash deficiency. Confirmation is offered of deficiency symptoms in maize by chemical tests. Similar reference is made to other cereals, to fruit trees, and to grape vines.

The illustrations are extremely valuable as indicative of potash deficiency. The color plates are excellent and will unquestionably prove most helpful to producers as well as to teachers and investigators. The text is given in three languages; namely, German, French, and English.

*Energiequellen der Welt.* By RUDOLF REGUL. Hanseatische Verlagsanstalt, Hamburg, Berlin, 1937. Pp. 78.

The major topics dealt with in this publication include an introduction to energy economics and statistics. The first part deals with the upbuilding and developments in the use of energy in the world. The second part deals with the materials employed in the development of energy for various purposes. Such topics as sources of energy, the utilization of energy, the consumption of energy, and the international exchange of energy carriers are considered by the author.

The subject discussed in this treatise is of a particularly timely character. The statesman, as well as the economist and industrialist, is intimately concerned with the resources of coal, mineral oils, water power, and wood. The general recognition of the rapid depletion of some of our energy resources has stimulated a search for new sources of energy. The statistical information offered by the author should prove helpful to all students of economics and of international trade.

*Rothamsted Experimental Station Report for 1936.* Gibbs & Danforth, Ltd., St. Albans, England, 1937. Pp. 294. Price 2/6.

The cumulative value of the long-term experiments conducted at the Rothamsted Experimental Station at Harpenden is apparent to every student of soils and soil management. The present report covers the activities for 1936, supplementing the interesting and helpful data which appeared in earlier reports. A short statement concerning this particular report—prepared at the Rothamsted Station—follows:

The Annual Report of the Rothamsted Experimental Station fills a special place in the literature of science applied to agriculture. It reaches research workers in soil science and plant nutrition all over the world, and is of special interest to scientific workers, advisory officers and students in this country. It outlines the present position of the various investigations on soil and fertilizer problems conducted at the Station, and gives in full the yield figures for 1936 obtained from some 120 experiments carried out at Rothamsted, Woburn and numerous commercial farms in various parts of England.

An important section summarises the results obtained in experiments on soil cultivation during the last 11 years. Contrary to the widely accepted view the results obtained up to the present indicate that under the conditions prevailing at Rothamsted, yields are not greatly dependent on the particular cultivation methods used, so long as the work is done at the right time. These trials must be continued but the figures already available are worth careful study. A preliminary discussion of the effects of fallowing on the yields of wheat on Broadbalk Field brings out the striking difference of behaviour between the starved and the fully manured plots. When the yield is poor, fallowing produces a large increase in yield; in the presence of nitrogenous manures the effect is much less and may even be harmful in the first year following. The benefit due to fallow appears to be only of one year duration as measured in the wheat crop. Experiments on the incorporation of raw straw with an accompanying dose of artificials show that handled in this way straw has so far produced much the same effect as dung or Adoo Compost. Other sections of importance deal with experiments on dried poultry manure and the effect of fertilisers on sugar beet.

Long period surveys of the work of certain departments have been a feature of recent reports. This year the summaries deal with Field Experiments, Fermentation, Insecticides, and Entomology.

JACOB G. LIPMAN



# STUDIES ON THE BEHAVIOR OF MANGANESE IN SOILS<sup>1</sup>

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Numerous studies (4, 6, 7) on the rôle and behavior of manganese in soils are presented in the literature. Some of the conditions affecting the solubility of manganese in the soil solution, such as pH and oxidizing-reducing states, have been rather clearly elucidated by various investigators (4, 6). The effect of liming and other fertilizer treatments on exchangeable manganese has been brought out in the work of Schollenberger and Dreibelbis (17), Mann (7), Willis (20), and Connor (4). Robinson (14) has pointed out that manganese may occur in soils largely as manganese dioxide concretions concentrated in the sand and silt fractions. On the other hand, he has shown that the bulk of the exchangeable manganese is located in the colloidal fraction. Gilligan (5) has pointed out that the electrodialyzable manganese content of limed soils is higher than that of unlimed soils.

The purpose of the present investigation was to study some of the factors governing the behavior of manganese in soils under definite treatment when subjected to salt extraction and electrodialysis, with the hope that the results would be helpful in the solution of soil and crop problems involving the use of manganese. All the soils studied, with the exception of Penn silt loam, were of Coastal Plain origin. For a study of the delivery rates of manganese during electrodialysis, cultivated soils from the following localities were used:

*Sassafras sandy loam:* 0"-6" depth, obtained from the Kilbourne Farm at the New Jersey Agricultural Experiment Station, New Brunswick, N. J.

*Sassafras sand:* 0"-6" depth, obtained near Hammonton, N. J.

*Collington loam:* 0"-6" depth, obtained outside Matawan, N. J. This field had been recently limed.

*Colts Neck loam:* 0"-6" depth, obtained near Colts Neck, N. J.

In addition to the studies on these soils further studies were carried out with certain soils which were later partially saturated with manganese. These samples consisted of the B horizon from the following two profiles:

*Sassafras loam:* obtained near Colonial Gardens, New Brunswick, N. J.

*Penn silt loam:* obtained from a road cut about 2 miles from Franklin Park on the road to Griggstown, N. J.

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<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

Certain limed and unlimed plot soils at the New Jersey Experiment Station were also investigated in connection with this problem. The soil on these plots was Sassafras loam and had received varying amounts of calcium limestone and dolimitic limestone at 5-year intervals for the last 25 years.

#### METHODS

The soils that were partially saturated with manganese were prepared by leaching 500 gm. of the soil with 10 liters of a normal solution of  $\text{MnCl}_2$  on a Büchner funnel using gentle suction. The soils were then washed with distilled water until free from chlorides, air-dried, and passed through a 2-mm. sieve.

Electrodialysis, cation exchange capacity, and ultimate pH determinations of the soil samples were carried out as reported elsewhere (12). Of the partially saturated manganese soils, however, a 25-gm. sample was used instead of the usual 100-gm. sample, and the period of electrodialysis was 38 hours.

Exchangeable manganese was obtained both by the normal ammonium acetate and 0.05N HCl methods.

Total manganese in the soils was determined by fusing with potassium bisulfate followed by the usual colorimetric periodate method (1, p. 8, par. 24).

In the extracts and certain dialyzates, interfering salts and organic matter were removed prior to the determination of manganese by the periodate method.

The manganese in the cathode dialyzates from the soils containing adsorbed manganese was determined gravimetrically by filtering off the hydrated manganese micelles and igniting to  $\text{Mn}_2\text{O}_3$ . Silica was removed by the addition of a few drops of hydrofluoric acid to the precipitate, followed by ignition to constant weight. In the case of the manganese soils that were treated with  $\text{Ca}(\text{OH})_2$ , it was necessary to remove calcium prior to igniting the hydrated manganese oxides. This was accomplished by leaching the filtered micelles from the cathode dialyzates with normal ammonium chloride solution until free from calcium.

#### SOME GENERAL OBSERVATIONS ON THE BEHAVIOR OF $\text{MnCl}_2$ AND ADSORBED MANGANESE IN SOILS UNDER ELECTRODIALYSIS

During the electrodialysis of a  $\text{MnCl}_2$  solution certain observations of importance were noted. Coincident with the passage of the electric current through the cell, a light brown floc of  $\text{Mn}(\text{OH})_2$  appeared in the cathode chamber. The pH in this compartment after 15 minutes of electrodialysis was between 9.0 and 9.2. Continuing the electrodialysis for a period of 1 hour brought the pH value of the catholyte to about 9.2–9.4. This pH range no doubt expresses the basicity of  $\text{Mn}(\text{OH})_2$ . The same observations were noted when soils containing adsorbed manganese were electrodialyzed. The precipitation of  $\text{Mn}(\text{OH})_2$  from solutions of manganese chloride begins at pH 8.4, according to Britton (3, p. 301), and does not reach completion until the pH is between 9

and 10. Schollenberger (15) observed that the addition of precipitated  $\text{Mn}(\text{OH})_2$  to soil had the same effect of increasing the pH in the suspensions as did equivalent  $\text{Ca}(\text{OH})_2$  up to pH 7.5, but further additions of  $\text{Mn}(\text{OH})_2$  did not result in higher pH values. Some later observations by the same author (16) suggest that this may have been because the manganese adsorbed by the soil above a certain level tended to become oxidized to forms inactive as base by exposure to the air.

Certain difficulties were encountered in determining the manganese electro-dialyzed from partially saturated manganese soils. When the determinations were based solely on the amount of manganese transported and precipitated in the cathode chamber, the results were always low. The low values were not due to the presence of large quantities of soluble manganese in the clear catholyte filtrate, but rather to a failure to determine the manganese which had precipitated in the parchment paper facing the cathode. In order to illustrate how the electro-dialyzed manganese was distributed in various parts of the cell, the following data are given on the electro-dialysis of Penn silt loam:

*Electrodialysis of Penn silt loam containing adsorbed manganese*

Total Mn by electro-dialysis . . . . .	10.23 m.e. per 100 gm. soil
Precipitated Mn micelles in catholyte . . . . .	9.94 " " " " "
Precipitated Mn in the parchment paper . . . . .	0.28 " " " " "
Soluble Mn in catholyte filtrate . . . . .	0.01 " " " " "

In the electro-dialysis of manganese soils that were treated with  $\text{Ca}(\text{OH})_2$ , greater quantities of Mn were found in the parchment paper (0.9–1.4 m.e.) than the values recorded above. In the electro-dialysis of soils, basoids and acidoids are also transported to the cathode (9, 18), and these would be weighed along with the  $\text{Mn}_3\text{O}_4$  precipitate. Silica was removed from the precipitate, however, by the addition of a few drops of hydrofluoric acid (loss in weight of precipitate from 100 gm. of soil was about 5–15 mgm.), and since only small quantities (0.5–3.0 mgm.) of  $\text{R}_2\text{O}_3$  are transported to the cathode (9, 12, 18), the effect of this transport would not seriously increase the values for the electro-dialyzable manganese.

A study was also made of the behavior of  $\text{Mn}(\text{OH})_2$  floc during electro-dialysis. For this purpose 20 m.e. of  $\text{MnCl}_2$  and 20 m.e. of  $\text{NaOH}$  were added to the center compartment of a standard Mattson cell. For comparative purposes a similar procedure was followed for an  $\text{Fe}(\text{OH})_3$  sol. The precipitates were allowed to stand over night in the cells, and the following day the cells were placed in the circuit, and the flocs were electro-dialyzed free from soluble ions. The following qualitative observations were noted:

A considerable quantity of both the manganese and iron hydroxide flocs were transported to the cathode, but the quantity of  $\text{Mn}(\text{OH})_2$  floc exceeded that of the  $\text{Fe}(\text{OH})_3$ .

As the quantity of soluble ions diminished, the transport of both flocs decreased.

The transport of the  $\text{Mn}(\text{OH})_2$  to the cathode continued in appreciable quantities even after the floc was free from soluble ions, whereas only traces of the  $\text{Fe}(\text{OH})_3$  floc migrated under these conditions.



The color of the transported  $\text{Mn}(\text{OH})_2$  micelles underwent a transition from a very light brown to a very dark brown during electrodialysis, indicating a possible change in the nature of the floc. This change in color of the floc is probably due to oxidation. It is possible that the course of the reaction and the color change are as follows:  $\text{Mn}(\text{OH})_2$  (white)  $\rightarrow$   $\text{MnO}_2$  (dark brown).

These observations, although qualitative in character, are important in the elucidation of the effect of lime on the transport of manganese from soils during electrodialysis, which will be discussed later.

It would be expected that the solubility of air-dry  $\text{Mn}(\text{OH})_2$  would be greater in 0.05 *N* HCl than in neutral normal ammonium acetate. An air-dried precipitate of  $\text{Mn}(\text{OH})_2$  was leached to 250 cc. with the extractants. The weight of the residue after this treatment was 0.0289 gm. by the 0.05 *N* HCl method and 0.0654 gm. by the normal ammonium acetate method. It is possible that oxidation and drying may affect the solubility of the floc, but in this study only relative solubilities are concerned.

#### RELEASE OF MANGANESE FROM SOME COASTAL PLAIN SOILS BY ELECTRODIALYSIS

The release of manganese from some soil colloids by electrodialysis has been studied by Mattson (8). In some respects the behavior of this cation is similar

TABLE 1

*Some data on Coastal Plain soils with respect to total and exchangeable manganese contents*  
Mn expressed in m.e. per 100 gm. soil

SOIL TYPE	FIELD pH	ULTIMATE pH	TOTAL Mn	EX-CHANGEABLE Mn BY <i>N</i> $\text{NH}_4\text{Ac}$	EX-CHANGEABLE Mn BY ELECTRODIALYSIS	TOTAL ELECTRODIALYZABLE Mn
Sassafras loam. . . . .	5.20	4.23	0.761	0.007	0.008	0.034
Sassafras sand. . . . .	6.35	4.18	0.226	0.007	0.006	0.013
Collington sandy loam. . . . .	5.77	3.67	0.423	0.007	0.005	0.032
Colts Neck loam. . . . .	4.83	4.15	1.155	0.029	0.026	0.098

to that of magnesium, iron, and aluminum, namely, that more of this cation is released in the later periods of electrodialysis than in the earlier stages. Four Coastal Plain soils were studied for this purpose. Before the delivery rates of manganese are discussed, some other important data on these soils are presented in table 1. The total manganese content as given in column 3 shows a variation from 0.226 m.e. per 100 gm. for Sassafras sand to 1.155 m.e. for Colts Neck loam. Exchangeable manganese by the normal ammonium acetate method on these soils was very low, ranging from 0.007 m.e. to 0.029 m.e. per 100 gm. soil. A good agreement between the exchangeable manganese by electrodialysis and by salt extraction may be noted in this table. The exchangeable manganese by electrodialysis may be defined as that manganese existing in the catholyte before the appearance of a large volume of sediment. This usually consists of the manganese appearing in the catholyte during the

0-8-hour period of electrodialysis. The manganese in this fraction exists primarily as soluble ions at pH values above 8.2. This fact is in line with McCool's findings that soluble manganese does exist in solutions of high pH values (6). The total electrodialyzable manganese represents the sum of the soluble manganese and the manganese transported as ionogenic complexes. It may be observed from the table that these values far exceed the exchangeable values.

Table 2 shows the delivery rates of manganese during electrodialysis from these four soils. Certain general conclusions may be drawn from these data. Simultaneously with the decrease in titrable bases, ionization and transport of manganese to the cathode increases to a maximum and then decreases. This maximum depends on the original base saturation of the soil, and with the soils studied it generally occurs between the 8-12- or the 12-16-hour periods of electrodialysis. The decrease after the maximum is reached is due, as pointed out previously (9, 12), to the formation of a sediment on the inner face of the cathode parchment paper. The factors influencing migration rates of the ionized complexes through this layer have been discussed elsewhere (9, 18). The foregoing facts, together with the work reported by Schollenberger (15) and Robinson (14), indicate quite definitely that manganese exists in two states in the soil, namely, as exchangeable ions adsorbed by the colloidal complex, and as higher oxides of manganese. The equilibrium between these two forms depends largely upon the conditions existing in the soil. Since it has been shown earlier in this paper that  $Mn(OH)_2$  may be transported to the cathode, and also that the partially hydrated oxides are more soluble under acid conditions, these facts may be utilized to explain why manganese as determined by electrodialysis is always greater than that extracted by neutral salts. During electrodialysis the soil is subjected to increasing acid conditions, and therefore the equilibrium between the two forms of manganese is shifted in the direction of the more soluble form. When this stage is reached manganese may be transported to the cathode as ions or it may combine with acidoids and be transported as ionogens. The migration of either form of ionized manganese to the cathode will lead to its precipitation because of the high pH in the catholyte.

An illustration of the effect of increasing the acidity of the Colts Neck loam below the ultimate pH on the mobility of manganese is shown in table 3. The acidity was increased by adding a suspension of electrodialyzed humic acid containing 2.89 gm. of solids to 100 gm. of soil. The preparation and properties of this humic acid have been discussed elsewhere (18). The addition of this material has increased the mobility of manganese from 0.098 to 0.342 m.e. Similar results were obtained for iron and aluminum by Mattson (9) and by Toth (18). Other investigators have shown that the addition of organic matter increases the solubility of manganese in soils.

In the light of the foregoing discussion, it appears that manganese behaves, in some respects, like the basoids, iron and aluminum. When soil colloids are

TABLE 2  
Release of manganese from some Coastal Plain soils during electro dialysis

PERIOD OF ELECTRODIALYSIS	TITRABLE BASES	Mn CONTENT OF CATHOLYTE	OBSERVATIONS ON CATHOLYTE
hours	m.e. *	m.e. *	
<i>Sassafras loam</i>			
0-4	0.616	0.0022	Clear
4-8	0.344	0.0056	Clear
8-12	0.243	0.0133	Slight sediment
12-16	0.020	0.0075	Slight sediment
16-20	0.000	0.0053	Very slight sediment
Total . .	1.223	0.0339	
<i>Sassafras sand</i>			
0-4	0.445	0.0002	Clear
4-8	0.222	0.0058	Very slight sediment
8-12	0.061	0.0038	Very slight sediment
12-16	0.044	0.0017	Very slight sediment
16-20	0.044	0.0011	Very slight sediment
20-28	0.010	0.0002	Clear
Total . . . .	0.826	0.0128	
<i>Collington sandy loam</i>			
0-4	1.698	0.0004	Clear
4-8	0.809	0.0047	Slight sediment
8-12	0.263	0.0156	Heavy sediment
12-16	0.081	0.0059	Slight sediment
16-20	0.044	0.0033	Slight sediment
20-28	0.020	0.0021	Very slight sediment
Total . . . . .	2.915	0.0320	
<i>Colts Neck loam</i>			
0-4	1.647	0.0010	Clear
4-8	0.788	0.0070	Clear
8-12	0.667	0.0170	Heavy sediment
12-16	0.303	0.0290	Heavy sediment
16-20	0.141	0.0220	Heavy sediment
20-28	0.060	0.0220	Heavy sediment
Total . . . . .	3.606	0.0980	

\* Per 100 gm. soil.

isoelectrically precipitated with iron and aluminum salts, a reduction in the cation exchange capacities of the colloids results. This is due to the combination of the basoid with the free valencies of the acidic fractions. In order to

determine whether manganese behaves in a like fashion, four sodium-saturated soil colloids (19) were isoelectrically precipitated with 1.5 millimoles of  $\text{MnCl}_2$  solution in a total volume of 1 liter [isoelectric precipitation of  $\text{Mn}(\text{OH})_2$  was at pH 7.05 (11)]. The exchange capacity determinations of the manganese and original colloids are given in table 4. It is to be noted from this table that no marked effect on the exchange capacity from the added manganese was obtained with the Colts Neck or Cecil colloid, and only a slight reduction, with the two more siliceous colloids, the Sharkey and Sassafras. This slight reduction in exchange capacity is negligible in comparison with the

TABLE 3  
*Electrodialysis of Colts Neck loam with 2.89 gm. of Humic acid in relation to electro-dialyzable manganese*

PERIOD OF ELECTRODIALYSIS	TITRABLE BASES	Mn CONTENT OF CATHOLYTE	OBSERVATIONS ON THE CATHOLYTE
<i>hours</i>	<i>m.e.*</i>	<i>m.e.*</i>	
0-4	1.819	0.004	Clear
4-8	1.233	0.009	Light sediment
8-12	0.626	0.064	Very heavy sediment
12-16	0.101	0.190	Very heavy sediment
16-20	0.000	0.075	Very heavy sediment
Total	3.779	0.342	

\* Per 100 gm. soil.

TABLE 4  
*Effect of isoelectric precipitation of manganese on the cation exchange capacity of soil colloids*

COLLOID	$\text{SiO}_2$ $\text{R}_2\text{O}_3$	CATION EXCHANGE CAPACITY	CATION EXCHANGE CAPACITY OF MANGANATED COLLOIDS	REDUCTION IN CATION EXCHANGE CAPACITY
		<i>m.e.*</i>	<i>m.e.*</i>	<i>m.e.*</i>
Sassafras . . . . .	3.37	0.206	0.181	0.025
Sharkey . . . . .	2.72	0.650	0.610	0.040
Cecil . . . . .	1.01	0.107	0.104	0.003
Colts Neck . . . . .	0.81	0.319	0.319	0.000

\* Per gram.

reduction in exchange capacity obtained by other investigators using iron and aluminum salts (10). This may be due to the instability of  $\text{Mn}(\text{OH})_2$  in alkaline solutions and to the effects of oxidation, leading to the formation of stable  $\text{MnO}_2$  rather than  $\text{Mn}(\text{OH})_2$ . Consequently with manganese in this form no direct combination between the acidoids can occur, and therefore no appreciable reduction in cation exchange capacity should be expected.

#### EFFECT OF LIMING ON MANGANESE IN SOILS

A clearer insight into the effect of lime on exchangeable and electro-dialyzable manganese was obtained by studying the effect of  $\text{Ca}(\text{OH})_2$  additions to soils

partially saturated with manganese. Two soils were used for this purpose: a Sassafras loam having an exchange capacity of 5.79 m.e. per 100 gm., and a Penn silt loam having an exchange capacity of 13.89 m.e. The former soil contained 3.20 m.e. of exchangeable manganese, and the latter, 10.04 m.e., as shown by normal ammonium acetate extractions after partial saturation with manganese by leaching with  $\text{MnCl}_2$  solution. These values were slightly higher as determined by extraction with 0.05 *N* HCl, being 3.53 and 10.78 m.e. respectively. By electrodialysis, the respective values were 3.89 and 10.23 m.e. The slightly higher values obtained by electrodialysis and by 0.05 *N* HCl are due to solubility effects upon the native manganese in these soils.

TABLE 5

*Relation between lime applications and exchangeable and electrodialyzable manganese on two soil types*

Ca(OH) <sub>2</sub> TREATMENT	pH OF SUPER- NATANT LIQUID	Ca(OH) <sub>2</sub> IN SUPER- NATANT LIQUID	Mn IN SUPER- NATANT LIQUID	EX- CHANGE- ABLE Mn BY N NH <sub>4</sub> ACETATE	EX- CHANGE- ABLE Mn BY 0.05 N HCl	ELECTRO- DIALYZ- ABLE Mn
		m.e.	m.e.	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.
<i>Sassafras loam</i>						
None . . . . .				3.20	3.53	3.89
Equivalent to one-half cation exchange capacity . . . . .	7.15	0.18	0.06	2.24	2.73	3.65
Equivalent to cation exchange capacity . . . . .	7.50	0.19	0.001	1.53	2.43	2.78
Equivalent to 2.0 times cation exchange capacity . . . . .	9.70	0.42	Trace	0.82	2.23	2.88
<i>Penn silt loam</i>						
None . . . . .				10.04	10.78	10.23
Equivalent to one-half cation exchange capacity . . . . .	6.90	0.15	0.001	6.42	8.62	10.00
Equivalent to cation exchange capacity . . . . .	8.07	0.23	Trace	2.75	6.46	6.60
Equivalent to 2.0 times cation exchange capacity . . . . .	11.90	2.14	Trace	1.46	5.20	6.61

The following procedure was used to study the effect of liming on the forms of manganese existing in the two soils partially saturated with manganese: 100 gm. of the soils were suspended in 750 cc. of solution containing  $\text{Ca(OH)}_2$  in three different amounts. These quantities of  $\text{Ca(OH)}_2$  corresponded to lime equivalents of one-half, one, and two times the cation exchange capacities of the soils. The soils were allowed to remain in contact with the solution for 2 days. At the end of this period, aliquots of the supernatant liquid were withdrawn, and determinations were made for soluble calcium, manganese, and pH. The soils were transferred to a large Büchner funnel, and the excess liquid was drawn off by suction. The soils were air dried and submitted to the normal ammonium acetate and the 0.05 *N* HCl extractions, as well as to electrodialysis.

The data for this experiment are reported in table 5. It may be seen that traces of manganese existed in the solutions even at pH values as high as 11.9. The exchangeable manganese by ammonium acetate decreased with increasing lime applications and pH. This is undoubtedly due to the exchange between the adsorbed manganese and calcium ions in the solution, resulting in precipitation of the former cation as insoluble  $Mn(OH)_2$  which may be oxidized to  $MnO_2$ . For example, with the lowest treatment of lime on Penn silt loam, exchangeable manganese decreased from 10.04 m.e. per 100 gm. to 6.42 m.e., and with the highest lime treatment, to 1.46 m.e. Sassafras loam exhibited similar reductions. The exchangeable manganese by the 0.05 *N* HCl method was always higher than that obtained with the neutral salt method, as may be noted in the table. This may be accounted for by the solvent effect of the acid extractant upon the precipitated manganese complexes. In every case where the exchangeable manganese by the neutral salt method decreased, the exchangeable manganese by the 0.05 *N* HCl method increased in relation to the lime treatment. This indicates that where more of the original exchangeable manganese was precipitated as the hydroxide with increasing increments of lime, the solvent action of the acid extractant was more marked.

The contents of electro dialyzable manganese from these limed soils were greater than the values obtained by the neutral salt or 0.05 *N* HCl methods. The reasons for these higher values have already been discussed. It is of interest to note, however, that a maximum of only 6.6 m.e. of manganese per 100 gm. Penn silt loam and 2.88 m.e. per 100 gm. Sassafras loam was obtained from the two higher lime treatments.

#### INFLUENCE OF CALCIUM LIMESTONE AND DOLOMITIC LIMESTONE ON MANGANESE IN FIELD SOILS

The distribution of manganese in certain field plots as affected by lime treatment has been discussed by Blair and Prince (2), who showed that the total manganese content of the  $A_p$  horizon is generally higher than that of the lower horizons. In tables 6 and 7 the data on the distribution of total, exchangeable, and electro dialyzable manganese in the surface and subsoils of certain plots treated with various forms and amounts of lime are recorded.

The total, exchangeable, and electro dialyzable manganese content of the surface soils was found to be greater than that of the subsoils. The data presented in an earlier publication (13) on the soils of these plots indicate a definite accumulation of iron and aluminum in the subsoils under podzolization processes. This fact would lead one to suspect that manganese is not being transported to the lower horizons in the profile but is accumulating at the surface. This behavior of manganese in the profile is in line with our previous discussion earlier in the paper and the fact that Robinson (14) was unable to distinguish any other forms of manganese in the soil but manganese dioxide and manganese as exchangeable ions.

It would seem from the data in tables 6 and 7 that an actual conservation of total manganese occurs in the soil with the lime treatment. As pointed out

previously (13), however, the general data on these field plots point to an inherent difference between the plots. The behavior of manganese in soil from other plots of this series does not show this effect. For example, the data from the duplicate plots corresponding to the dolomitic limestone series

TABLE 6

*Effect of limestone on exchangeable and electrodialyzable manganese in Sassafras loam*

PLOT NUMBER	LIMESTONE TREATMENT	FIELD pH	ULTIMATE pH	TOTAL Mn	EXCHANGEABLE Mn BY N NH <sub>4</sub> Ac	Mn BY ELECTRODI-ALYSIS
	lbs.*			m.e.†	m.e.†	m.e.†
21 Top . . . . .	None	5.03	4.42	0.761	0.030	0.034
22 Top . . . . .	1000	5.27	4.22	0.902	0.029	0.091
23 Top . . . . .	2000	5.62	4.44	0.987	0.023	0.084
24 Top . . . . .	4000	6.36	4.33	1.268	0.029	0.156
21 Sub . . . . .	None	5.24	4.42	0.705	0.012	0.029
22 Sub . . . . .	1000	5.58	4.33	0.507	0.007	0.031
23 Sub . . . . .	2000	5.96	4.55	0.536	0.012	0.026
24 Sub . . . . .	4000	6.68	4.47	0.902	0.009	0.068

\* Per acre.

† Per 100 gm. soil.

TABLE 7

*Effect of dolomitic limestone on exchangeable and electrodialyzable manganese in Sassafras loam*

PLOT NUMBER	DOLOMITIC LIMESTONE TREATMENT	FIELD pH	ULTIMATE pH	TOTAL Mn	EXCHANGEABLE Mn BY N NH <sub>4</sub> Ac	Mn BY ELECTRODI-ALYSIS
	lbs.*			m.e.†	m.e.†	m.e.†
21 Top . . . . .	None	5.03	4.42	0.761	0.030	0.034
25 Top . . . . .	1000	5.44	4.45	1.212	0.035	0.054
26 Top . . . . .	2000	5.87	4.33	1.353	0.015	0.077
27 Top . . . . .	4000	6.84	4.31	1.466	0.025	0.146
21 Sub . . . . .	None	5.24	4.42	0.705	0.012	0.029
25 Sub . . . . .	1000	5.73	4.39	0.902	0.016	0.041
26 Sub . . . . .	2000	6.26	4.45	0.959	0.009	0.032
27 Sub . . . . .	4000	7.08	4.43	1.000	0.014	0.052

\* Per acre.

† Per 100 gm. soil.

described in table 7 showed a uniform content of total manganese, namely, 1.10 m.e. per 100 gm.

The exchangeable manganese content of the soils did not indicate a definite correlation with the lime treatment either in the surface or in the subsoils. The values for exchangeable manganese ranged from 0.007 to 0.03 m.e. per 100 gm. The lack of correlation between the data from the field and that obtained in the laboratory, where the influence of Ca(OH)<sub>2</sub> addition upon

exchangeable manganese was studied, may be due to the fact that under field conditions it is impossible to control all factors rigidly.

The electrodialyzable manganese generally increased with the limestone applications. Gilligan (5) has noted that limed soils contain more electrodialyzable manganese than unlimed soils, and the results in tables 6 and 7 are in line with his findings. An examination of the data in tables 6 and 7 would seem to indicate a correlation between the total and electrodialyzable manganese. That no such correlation exists may be seen from the electrodialyzable manganese content of certain plots that have a fairly uniform content of total manganese. The data that follow are given for only the surface soils of the corresponding series reported in table 7:

DOLOMITIC LIMESTONE TREATMENT	PLOT NUMBER	TOTAL Mn	ELECTRODIALYZABLE Mn
<i>lbs./A.</i>		<i>m.e./100 gm.</i>	<i>m.e./100 gm.</i>
None	21	0.76	0.034
1000	39	1.10	0.027
2000	40	1.10	0.042
4000	41	1.10	0.094

The behavior of the electrodialyzable manganese on these field soils is in line with the data presented in table 5 where a similar study was made under laboratory conditions.

#### SUMMARY

The behavior of manganese in soils under laboratory and field conditions was studied.

An attempt was made to clarify the electrodialytic behavior of solutions of  $MnCl_2$  and soils containing adsorbed manganese. It was shown that adsorbed manganese can be released quantitatively from soils by electrodialysis.

The release of manganese from some cultivated Coastal Plain soils of New Jersey by electrodialysis was studied. A similarity was observed between the release of manganese, iron, aluminum, and magnesium under these conditions. The mobility of manganese increased in the later stages of electrodialysis as the pH of the soil decreased. The transport of manganese was primarily as ionogens rather than as ions.

Manganese appeared to exist in the soils as exchangeable ions and ionogenic complexes. The equilibrium between these two forms of manganese was affected by soil conditions. The addition of humic acid to Colts Neck loam resulted in a greater release of manganese.

The isoelectric precipitation of  $Mn(OH)_2$  with sodium-saturated soil colloids did not reduce to any extent the cation exchange capacity of the colloids.

Soils that were partially saturated with manganese were used to study the effect of lime on exchangeable and electrodialyzable manganese. It was shown that as the lime applications increased the exchangeable manganese decreased. The values for the electrodialyzable manganese always exceeded



the exchangeable. This was due to the fact that electro dialyzable manganese represented the sum of exchangeable manganese and manganese transported as ionogenic complexes. It was also shown that manganese in the latter form is nonexchangeable but is soluble to some degree in 0.05 *N* HCl.

The data obtained with field soils were interpreted from the viewpoint of the laboratory experiments and confirmed the laboratory findings. It was also pointed out that the surface soils contained more total manganese than did the subsoils.

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# THE MOVEMENT OF WATER IN HEAVY SOILS AFTER IRRIGATION

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The theory of diffusion of water through soil (2), developed in connection with the drainage of heavy clay soils in humid climates (7), has been shown to be in agreement with the behavior observed (3) in artificially prepared columns of soil material investigated by various workers (1, 8, 9). The application of the theory to similar soils in more arid climates where irrigation is the rule, is of special interest. Not only is the computation of penetration of water of direct importance, but the zones of irrigation provide the most favorable conditions for testing the theory by experiments in the field. It need hardly be stressed that such field experiments are essential, since it is impossible to prepare adequate lysimeters at reasonable cost without disturbing the natural structure of such soils and thereby profoundly modifying their drainage properties. Field experiments are not easy in a region of variable and only approximately predictable weather, such as the British Isles, because the theory can be developed, on account of mathematical difficulty, only for certain steady surface conditions. Moisture movements in heavy soils are so slow that such steady conditions must be maintained for a considerable length of time before one can observe changes of moisture content which are large in comparison with the errors involved. The controlled applications of water during periods of very settled weather, associated with irrigation, render the regions where such operations are carried out peculiarly suitable for our purpose. They have the added advantage that the application of a large quantity of water in a short time produces a moisture profile having a steep gradient at considerable depth. This means, as we shall see, that water movements are to be observed in a medium which is fairly uniform and free from surface disturbances.

Fortunately, a region of the type described, enjoying well-defined seasons and steady weather, has been the home of experiments on moisture movements in clay soils (4), and data of a nature suitable for the application of diffusion theory are available. Greene, working in the Eastern Gezira where the soil is a heavy clay of alkaline reaction, has published a number of moisture profiles in connection with irrigation practice, and some of these have been chosen as the material for the present discussion.

<sup>1</sup> It is a pleasure to acknowledge the unstinted help afforded me by H. Greene and O. W. Snow, who have freely put at my disposal unpublished data from the Agricultural Research Station at Wad Medani, in the Eastern Gezira.

The basis of the diffusion theory, recapitulated, is the assumption that the rate of flow of soil moisture at a given point in a given direction is proportional to the gradient of the moisture profile in that direction. The justification for this assumption has been previously discussed (2, 7). Thus if one expresses the mass of soil water per unit volume of soil as a fraction  $c$  of the mass of dry matter,  $\sigma$ , per unit volume, then the rate of flow,  $\frac{\partial Q}{\partial t}$ , in the direction  $x$  is proportional to  $\frac{\partial c}{\partial x}$ , i.e.,

$$\frac{\partial Q}{\partial t} = -k \frac{\partial c}{\partial x} \dots \dots \dots (A)$$

where  $k$  is a constant of proportionality and is called the "diffusion coefficient." Starting with a knowledge of  $k$ ,  $\sigma$ , and the initial moisture profile, however complicated, we can calculate the subsequent moisture profile at any time for certain conditions of water control. In particular, if we identify  $x$  with depth and assume horizontal planes to be surfaces of equal moisture content, and imagine that the soil surface is maintained at constant wetness (for example, at saturation by means of irrigation or at air-dryness by rapid evaporation), then the moisture profile  $c_t$  at time  $t$  is given by the expression:

$$c_t = c_s + \sum_n \left( \frac{2}{l} e^{-\frac{k}{\sigma} \left( \frac{n\pi}{2l} \right)^2 t} \int_0^l (c_0 - c_s) \sin \frac{n\pi x}{2l} dx \right) \sin \frac{n\pi x}{2l} \dots (B)$$

$$(n = 1, 3, 5, 7, \dots)$$

where  $c_s$  is the constant surface moisture content,  $c_0$  the initial profile, and  $l$  is the total depth of the soil in which water diffusion is taking place.

If we assume, instead, that there is no arrival or departure of water from the soil as a whole, but only redistribution of such water as is already in it, we have now:

$$c_t = \frac{1}{l} \int_0^l c_0 dx + \sum_n \left( \frac{2}{l} e^{-\frac{k}{\sigma} \left( \frac{n\pi}{l} \right)^2 t} \int_0^l c_0 \cos \frac{n\pi x}{l} dx \right) \cos \frac{n\pi x}{l} \dots (C)$$

$$(n = 1, 2, 3, 4, \dots)$$

. The conditions leading to equation (B) are of importance in connection with drainage in humid climates, when rainfall maintains the surface of heavy soil in a state approximating saturation, and also in arid climates during the period following irrigation, when the heat from the sun tends to maintain the surface, at least during the day, in a condition of air-dryness. Hence, using the appropriate equation, we can calculate a moisture profile for comparison with the one observed at the end of the given interval or intervals of time, and the extent of the agreement between the two is the evidence for the soundness of the theory. It will be seen that the analysis involves the evaluation of certain

definite integrals of functions of the depth, and the range over which these must be taken is, to be rigid, the whole depth of the soil deposit. In practice we make only negligible errors in limiting the range to that depth in which water movement is known to be greater than the errors of measurement.

#### EXPERIMENTAL DATA

Two of Greene's sets of experiments contain sufficient material of the nature required for our purposes. These are (a) the investigation of the soil-moisture profiles at various dates after irrigation and (b) the examination of the effect of applications of gypsum on the depth of penetration of water. The curves are not entirely satisfactory for our purpose, since the experiments were carried out with other ends in view, but we shall see that they are adequate when one considers the approximate sort of agreement with theory which can be legitimately expected from such a nonuniform medium as a field soil 6 or more feet deep. In each experiment the moisture content at various depths shortly after irrigation is given, and from this information the moisture profiles were obtained by drawing the smoothest possible curves through the points given by plotting moisture content against depth. These are shown as the solid line curves in figures 1 to 5, in which the experimental points are generally omitted in order to avoid confusion with observed values on subsequent occasions.

Starting with these initial profiles, we must, in calculating subsequent profiles, first decide upon the proper conditions to be assigned to the surface. It must be admitted that the actual state of affairs is so complicated that a rigid solution of the diffusion equations is out of the question. We must choose conditions which permit of a solution if we are to progress farther, yet these must be a sufficiently good approximation to the truth if the calculations are to be of more than academic interest. Immediately following irrigation, when the soil at the surface is very wet, it is likely that the rate of evaporation is limited by the rate of absorption of heat from the sun, and the appropriate boundary condition is then that the rate of loss of water from the surface, averaged over each day, is constant. This state of affairs cannot last very long, and must be succeeded by one in which the rate of evaporation is limited by the maximum rate at which water can reach the surface from the soil below. Because of the slowness of water movements in heavy soils, this maximum rate may be so low that the sun is able to maintain the surface in a state of air-dryness; the gradually decreasing rate at which water reaches the surface is just balanced by the rate at which it leaves the surface in the form of vapor. When these latter conditions set in, the pressure of the water vapor at the surface must be low, and consequently evaporation can take place within the soil, the vapor thus produced diffusing upward through the drier layers (down the vapor-pressure gradient) and so to the outside air. In this way the actual water loss is doubtless greater than that accounted for by diffusion of water in the liquid state, with the assumed boundary conditions. Hence if we assume, as the general trend of the published profiles would lead us to suppose,

that the soil surface is maintained throughout the drying period in a state of air-dryness, we shall probably overestimate the loss of water in the early part of the period and underestimate it in the latter part. We may, therefore, expect our calculations to provide a final profile which is not very far from the truth, the more so because, as will be shown, rather large variations in the surface conditions have only a minor effect on the changes in the moisture profile at considerable depth, where our interest is chiefly centered.

Our arguments lead us, therefore, to choose equation (B) as that appropriate to the case. The only question remaining to be settled is the correct value to be assigned to the surface moisture content,  $c_s$ . Greene (4) gives figures of 14 per cent and 6 per cent respectively for the hygroscopic coefficient and air-

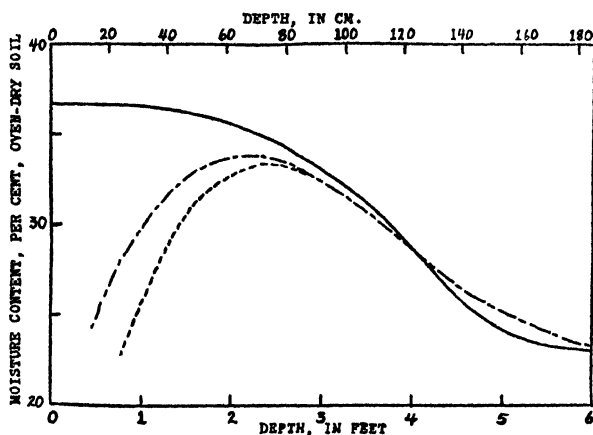


FIG. 1. MOISTURE PROFILES ILLUSTRATING EFFECT OF DIFFERENT SURFACE CONDITIONS ON THE CALCULATED PROFILES FOR EASTERN GEZIRA SOIL

- Initial profile.
- - - - - Calculated subsequent profile, surface maintained at 14 per cent moisture.
- · - · - Calculated subsequent profile, surface maintained at 0 per cent moisture.

It will be observed that the difference is negligible below about 2 feet.

dry moisture content of Gezira soil. It might be thought that the surface soil, being in contact with moister lower soil, should not dry out to such a low moisture content as the air-dry value, yet one at least of the observed profiles tends to a moisture content of zero at the surface. Because of this uncertainty, calculations were made to illustrate the difference between the effects of maintaining the surface at 14 per cent moisture and at zero moisture. The result is shown in figure 1, the initial profile being that observed by Greene 6 days after irrigation (4, fig. III) and with a trial value of  $\frac{k}{\sigma}$ . When the true value of  $\frac{k}{\sigma}$  finally decided upon is taken, the calculated profiles correspond to a time interval of about 40 days. It will be seen that the difference to be expected

is confined to the top 2 feet, a region in which we are not primarily interested. Hence it is not a serious matter if we make an indifferent judgment of the surface conditions within the possible limits. In the present paper a value of zero has been assigned to  $c$ , where this has seemed to be the case, and a value of 14 per cent where this has been judged proper; in no case does this difference affect the results except near the surface.

#### COMPARISON OF OBSERVED AND CALCULATED PROFILES

We deal first with the profiles showing the movement of water in plots receiving various applications of gypsum. The control plots are neglected

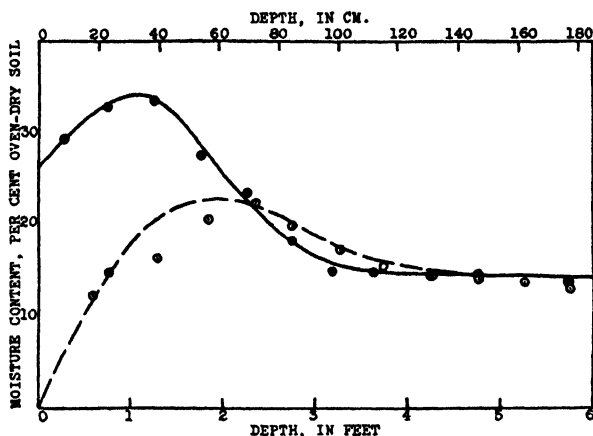


FIG. 2. COMPARISON BETWEEN OBSERVED AND CALCULATED MOISTURE PROFILES FOR GEZIRA SOIL TO WHICH 1 TON OF GYPSUM PER ACRE HAD BEEN APPLIED

Values of constants used for the calculations are  $\frac{k}{\sigma} = 3.0$ ,  $c_s = 0$ .

- Initial profile, April 1927.
- ● ● Observed points from which the initial profile was drawn.
- - - Calculated profile, October 1927.
- ○ ○ Observed values, October 1927.

because, in the untreated soil, the steeply sloping parts of the initial profile where moisture movements may be expected to be at a maximum are within the top 2 feet, and hence the moisture movements in which we are interested take place in a region which is subjected to the masking influences and the uncertainties of calculation which we have discussed. In figure 2 is shown the initial profile, taken in April 1927, for the plots to which 1 ton of gypsum per acre had been applied, together with the experimental points from which the initial profile was drawn. The profile calculated for October 1927 is shown together with the observed points for this date for comparison. Greene also publishes a profile taken in December 1927, but it is not profitable to attempt to calculate a profile because water was applied shortly before this profile was

observed, the surface conditions thereby being drastically changed. This point will again be referred to in the discussion. It is sufficient to remark here that this December profile is consistent with the view that the deeper soil had gained more water at the expense of the upper layers, in accordance with the diffusion laws, but the subsequent irrigation had made good the losses suffered by these upper regions.

The behavior of plots having a dressing of 4 tons of gypsum per acre differs from that of all the others in that the soil at all depths loses moisture, instead of the dry lower soil's gaining at the expense of the upper moistened soil. If we examine figure 3, we see that the shape of the October profile is what we should expect but that there is a displacement bringing it wholly below the

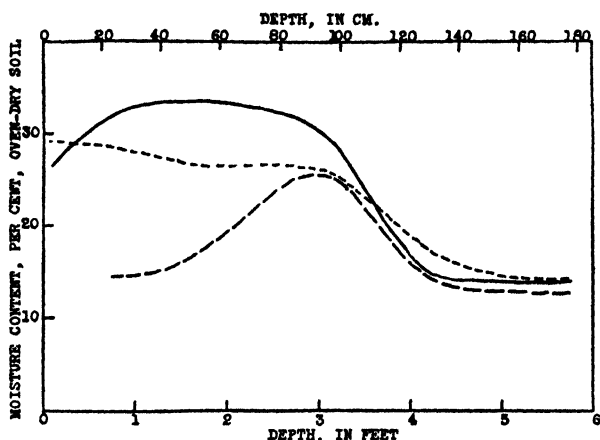


FIG. 3. MOISTURE PROFILES FOR GEZIRA SOIL TO WHICH 4 TONS OF GYPSUM PER ACRE HAD BEEN APPLIED

- Initial profile, April 1927.
- - - Subsequent profile, October 1927.
- · - · Subsequent profile, December 1927.

initial April profile instead of there being an intersection at a depth of about 3.5 feet and an asymptotic approach at greater depth. Calculations for this anomalous case were not made, but by comparison with the calculated curves in figures 2 and 4 it can be seen that the theoretical profile would be closely similar to the observed December profile. This also will be discussed later, but the anomaly may be no greater than can be accounted for by experimental error, since there was only fourfold replication of plots and the changes of moisture content in which we are interested do not amount to more than 2 or 3 per cent of the weight of dry matter.

In figure 4 is shown the behavior of the plots to which 10 tons of gypsum per acre was applied. The previous remarks apply here. This calculated profile is also in rather better agreement with the December profile than with that for

April, for which it was computed. The bodily shift of the April profile is not so pronounced, however, as in figure 3. The value adopted for  $\frac{k}{\sigma}$  in the foregoing calculated profiles was 3.0, where the units of length, mass, and time are the centimeter, the gram, and the day respectively.

A more stringent test of the theory is provided by figure 5. Here, starting with a profile taken 6 days after irrigation, two subsequent profiles can be calculated and compared with those observed, one being for a short time-interval (26 days after irrigation) and the other being observed 120 days after irrigation. The sampling, even though carried to a depth of 6 feet, did not

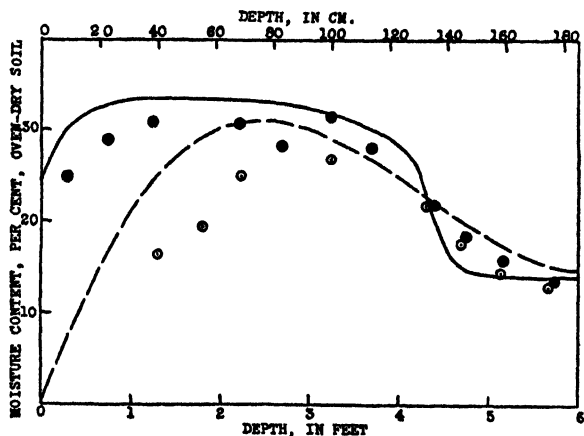


FIG. 4. COMPARISON BETWEEN OBSERVED AND CALCULATED MOISTURE PROFILES FOR GEZIRA SOIL TO WHICH 10 TONS OF GYPSUM PER ACRE HAD BEEN APPLIED

The observed points from which the initial profile has been drawn are omitted to avoid confusion.  $\frac{k}{\sigma} = 3.0$ ,  $c_s = 0$ .

- Initial profile, April 1927.
- - - - - Calculated profile, October 1927.
- ○ ○ Observed values, October 1927.
- ● ● Observed values, December 1927.

reach a region where moisture redistribution was negligible. It was therefore necessary to extrapolate the initial profile to a depth of 12 feet (366 cm.) and to a moisture content which seemed reasonable and probable. This extrapolation to a moisture content of 22 per cent at 12 feet is merely a necessity for the calculations and is of no interest in the discussion; it is therefore not shown in figure 5, which ends at the limit of observations, at a depth of 6 feet. The experiments were carried out on good soil at the Gezira Research Farm, whereas the preceding ones were on poor soil at Ganib. It was accordingly found necessary to choose a new value for  $\frac{k}{\sigma}$  for this soil, and by trial and error a value



of 16.0 was selected. It will be seen that the agreement between observed and calculated profiles is very fair below a depth of about 3 feet. It is possible that agreement extends upwards into the second foot from the surface, since the depression in the observed profiles, which occurs in the third foot through-

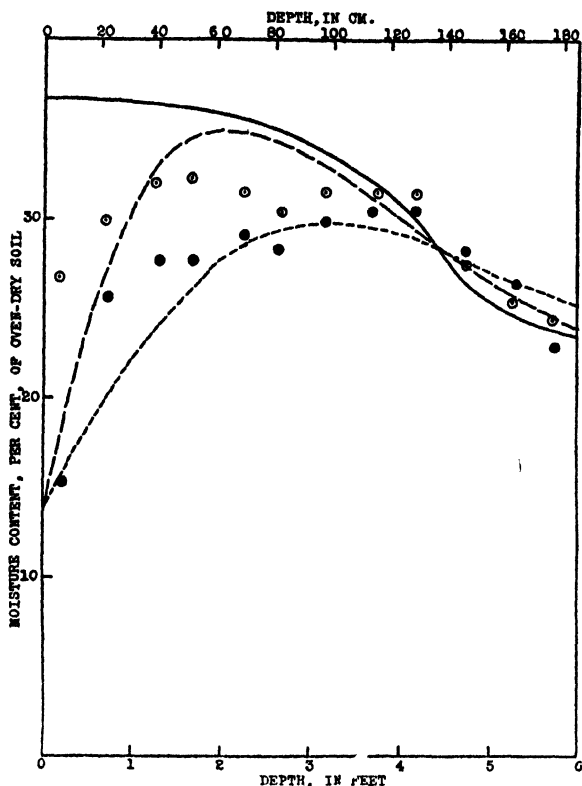


FIG. 5. COMPARISON BETWEEN OBSERVED AND CALCULATED MOISTURE PROFILES AT VARIOUS INTERVALS AFTER IRRIGATION

$\frac{k}{\sigma} = 16.0$ ,  $c_s = 14.0$  per cent.

- Initial profile, 6 days after irrigation.
- - - - - Calculated profile, 26 days after irrigation.
- ○ ○ Observed values, 26 days after irrigation.
- ..... Calculated profile 120 days after irrigation.
- ● ● Observed values 120 days after irrigation.

out the series, is due to the fact that the moisture contents are expressed as a percentage of the mass of dry soil matter, and the density of this, according to Greene, reaches a maximum in the third foot. If due consideration is given to the long intervals of time involved and the consequent possibility of changes of atmospheric conditions during the experiment (the experiments of figures 2

to 4 include, in fact, the summer rains in the "drying" period), to the fact that we are applying a theory developed for a homogeneous medium to a field soil and not to a laboratory mixture of artificial homogeneity, and finally to the fact that measurements of moisture profiles are subject to considerable errors, it would seem that the general agreement between observation and theory may be regarded as satisfactory.

#### DISCUSSION

The movements of water with which we have been dealing are of interest in connection with irrigation mainly in the study of the slow penetration during the long period following flooding. During the early part of the flood period, when the greater part of the water is taken up by the soil but does not penetrate much below the surface zone, movement is rapid and obeys other than diffusion laws. Water is applied when the soil is dry and therefore cracked, in places to a great depth. The first applications are observed to rush down these cracks under the force of gravity and presumably to spread almost equally quickly into the minor cracks and interspaces between the clods and crumbs. As this water is taken up, the soil swells, eventually the water passages close, and further movements are of the slow diffusion type. The mechanism by which the soil aggregates absorb the water from the interspaces may, of course, be of a diffusion nature, but this final stage is of only minor importance; it remains true that the presence of the water at the depth at which it is absorbed into the soil is accounted for by mass movement down the cracks under the force of gravity. When this early period is over and the swelling has closed the cracks, we may expect to observe further and much slower mass movements from one depth to another due to diffusion, unmasked by the rapid gravitational movements.

The behavior of gypsum as a soil improver, as indicated in figures 2 to 4, may be examined in the light of these observations. We first notice that the same value of the coefficient of diffusion holds for all the various applications of gypsum, and consequently that the slow penetration is in no way improved by such applications. The most obvious effect is on the rapid uptake of water during flooding, and here we see that increasingly heavy dressings of gypsum have the effect of steepening the "step" in the moisture profile and of shifting it to greater depths. Israelsen (5) has shown that such differences are characteristic of the change from heavy to light soil. It may be that replacement of the sodium, which occurs in the Gezira soils in notable quantities, by the calcium ion is accompanied by oriented coagulation, as has been suggested by Marshall (6), and an increase in size of the primary particles of the clay fraction; but, in any case, it is known that the calcium clay is more stable and swells less than does clay which contains appreciable quantities of exchangeable sodium. Hence crumbs and aggregates in general would tend to be more stable and the cracks and interspaces more persistent. In terms of coagulation, the closer binding of the clay particles has eliminated some of the minute

pore spaces in which diffusion occurs to the benefit of the major spaces. The cracks provide direct passages between the deeper soil and the outside air, particularly when the drying of the soil has caused the cracks to open slightly; and hence we must admit the possibility, as we have seen, of water loss, even at depth, by direct evaporation. At the same time the cracks, being chiefly in the vertical direction, would not tend to prevent the movement of water from one depth to another by diffusion; hence, we might expect two superimposed effects.

Examination of figures 2 to 4 shows that the observed water movements are consistent with the view of two superimposed effects outlined. The soil to which little gypsum was added gives moisture profiles which are in excellent agreement with the profiles calculated from the simple theory. With heavier dressings, however, there is a loss of moisture throughout the profile during the period April–October, in addition to a redistribution in accordance with diffusion laws. The effect is to give a profile which agrees in shape with the calculated one but is displaced downwards (i.e., in the direction of dryness). This loss must be accompanied by shrinking and cracking of the soil, so that reflooding might be expected to make good this loss almost instantaneously. The December profiles, taken shortly after such a reflooding, shows that this indeed happens, the whole curve of the profile being shifted to be in better agreement with that calculated. There is a rapid response to flooding even at a depth of 5 or 6 feet, whereas the first flooding penetrated quickly only to a depth of 3 or 4 feet. Behavior in the upper 2 feet is, as we have shown, wholly outside the scope of the simple theory.

In figure 5 we have omitted the profile observed 256 days after irrigation because the loss of moisture throughout the whole depth due to evaporation outweighs changes due to diffusion. The importance of the curves shown lies in their evidence of the continuous nature of diffusion. There is no indication of a final steady state differing from uniformity of moisture content, as has sometimes been supposed. A progressive movement of moisture takes place from the wetter to the drier soil. The actual value of the coefficient of diffusion may change with moisture content, i.e., it might have been possible to obtain better agreement between the calculated and observed profiles for the 26-day and 120-day periods separately by adopting a different value for each case, but the agreement shown indicates that such a change cannot be considerable in the range of moisture contents found under field conditions.

#### SUMMARY

An application of the theory of diffusion of water in heavy soils has been made to observations taken under irrigation conditions. It is shown that diffusion can account for the slow movements after irrigation and can be important in soil amelioration, but that during flooding such movements are masked by the more rapid gravitational movement.

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# A FIELD OUTFIT FOR DETERMINING THE MOISTURE CONTENT OF SOILS<sup>1</sup>

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It has been shown<sup>2</sup> that the moisture content of mineral soils containing less than 11 per cent of organic matter can be determined accurately and rapidly by means of the burning-alcohol method. In a series of comparative studies it was definitely proved that for such soils this method is as accurate as the standard oven-drying method, and that with the burning-alcohol method the moisture content of sands can be determined in from 5 to 10 minutes, of loams in from 10 to 20 minutes, and of clays in from 10 to 35 minutes, depending on their water content and their permeability to alcohol. In the report offering the method, technique and experimental data showing accuracy were presented. No attempt was made to apply the method to field conditions.

The method has since received further study with the object of applying it to field conditions. It is the purpose of this paper to present a field outfit that has been devised, by means of which the burning-alcohol method can be conveniently used to determine the moisture content of soils under field conditions.

## DESCRIPTION OF OUTFIT

This field outfit is shown in plate 1. It is a box 26 inches high 16 inches wide, and 7 inches deep, made of light galvanized iron and having two compartments. The lower compartment is a container for the necessary equipment. Its door consists of a metal sheet which slides from right to left in grooves. The upper compartment serves chiefly for housing the triple beam balance and protecting it from the wind. The two sliding doors to this compartment have glass windows which allow the operator to see and to adjust the weights accurately and which at the same time protect the balance from the wind. The glass is synthetic and is very light in weight and resistant to breaking. When the outfit is being carried, a metal sheet slides over the doors to protect the glass windows as well as to hold them in place. On the top of the box is a groove into which is inserted the door to the lower compartment, and

<sup>1</sup> Authorized for publication by the director as journal article No. 321 n.s.

<sup>2</sup> Bouyoucos, G. J. 1937 Evaporating the water with burning alcohol as a rapid means of determining moisture content of soil. *Soil Sci.* 44: 377-383.

thus is formed a platform where the soils can be dried by the burning-alcohol procedure.

For use in connection with this field outfit, a high-grade triple beam balance<sup>3</sup> is recommended. The balance is held firmly in place in the compartment; and since it is well protected from the wind, it functions with as high a degree of accuracy as it does in the laboratory.

The box when standing on the ground, is high enough for the comfortable operation of the balance by a person of normal height seated on a camp stool. On the other hand, various arrangements could be made to raise the box to suit the operator's comfort and convenience.

The soils are dried by means of burning alcohol, in a set of two cups, as shown in the lower compartment of the box (pl. 1, fig. 1). The smaller cup is made of copper, and the larger one of aluminum. The smaller cup is 2 inches in diameter,  $\frac{3}{4}$  inch deep, with perforated bottom, and resting on four legs  $\frac{3}{8}$  inch high. The larger cup is 3 inches in diameter, 1 inch deep, and has a solid bottom. The smaller cup, which contains the soil, is always kept in the larger cup in order that no soil will be lost during treatment with the alcohol and during weighing.

#### PROCEDURE

The procedure for making a moisture determination consists, first, of laying a filter paper in the bottom of the smaller cup, placing this cup in the larger one, and weighing them together. During the entire procedure the cups are always kept one inside the other and are always weighed together as a single unit. A layer of soil about  $\frac{1}{2}$  inch thick, amounting to about 20–30 gm., is placed in the small cup, and the cups are weighed again. About 25 cc. of pure methyl alcohol is then poured gradually on top of the soil layer, and after most of it has drained through the soil, it is ignited. After the alcohol is burned and the flame goes out, the cups are weighed a third time. In order to be certain that all the water in the soil is expelled, about 10 cc. more alcohol is poured into the large cup and burned, and the cups are again weighed. This procedure of burning small quantities of alcohol in the large cup and of reweighing is repeated until the weight becomes constant. As a rule, more than two alcohol burnings are necessary to dry the soil completely. Several burnings are necessary for a soil of high moisture content. With such soils, it is not necessary to weigh the cups until several portions of alcohol are burned.

It was found experimentally that the soil can be dried more rapidly, and with considerably less consumption of alcohol, by adding several small amounts of alcohol than by adding a very large amount at the outset. This is partly due to the fact that when a small amount is used the flame tends to get under the soil cup and heat the soil. Since the alcohol is not explosive, it can be poured into the large cup while there is still some flame. In order to eliminate the tedious procedure of measuring out the small portions of alcohol, a special

<sup>3</sup> Catalog no. 1966, Arthur Thomas & Co.

mark has been made in the large cup to indicate a 10 cc. volume of alcohol. The supply of alcohol, therefore, can be kept in a bottle, and by means of a syphon arrangement, the small additions of alcohol can be measured into the cup.

#### COMMENTS

As shown in the first report, the moisture content of mineral soils containing less than 11 per cent of organic matter can be determined as accurately by the burning-alcohol method as by the standard oven-drying method. This follows logically from the fact that the soil is repeatedly dried with burning alcohol until its weight becomes constant.

In the field, as in the laboratory, the rapidity of the method for determining soil moisture depends upon the water content of the soil and upon the extent to which the alcohol extracts the water as it percolates through the soil. It is quicker to evaporate the water when it is dissolved in alcohol than when it is in the soil. To determine the moisture content of soils that are readily permeable, such as the sands, and even the clays in the granular condition and of low moisture content, takes about 5 to 15 minutes, including the time for weighing. Soils that have a very high moisture content, especially if they are impermeable, such as heavy puddled clays, require from 10 to 35 minutes for moisture determination. On the other hand, work may be carried forward on a number of soils at the same time, as the procedure does not require constant attention.

#### SUMMARY

An outfit has been devised, which can easily be carried into the field, for the accurate and rapid determination of the moisture content of soils by means of burning alcohol.



## PLATE 1

FIELD OUTFIT FOR DETERMINING MOISTURE CONTENT OF SOILS BY THE BURNING-ALCOHOL  
METHOD

FIG. 1. Open view of the box with glass windows.

FIG. 2. Closed view of box.

(Manufactured and handled by the Wood and Metal Products Company, Bloomfield Hills, Michigan.)

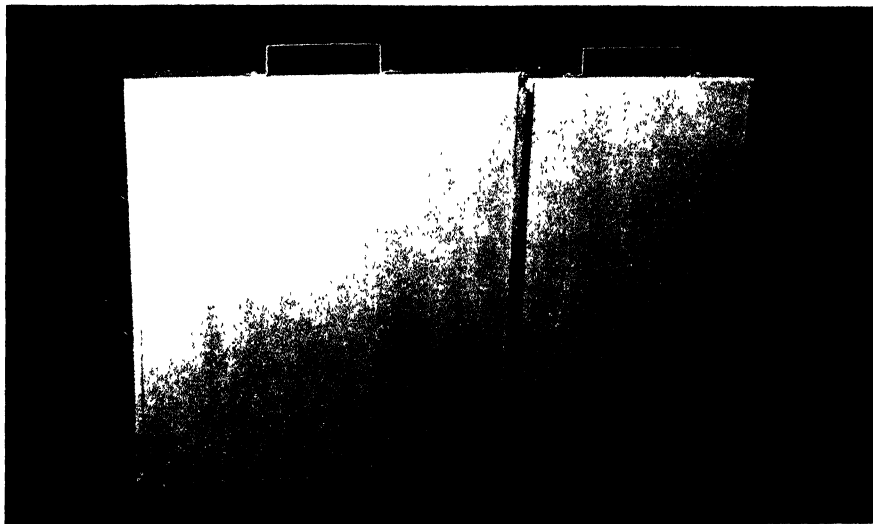


FIG. 2

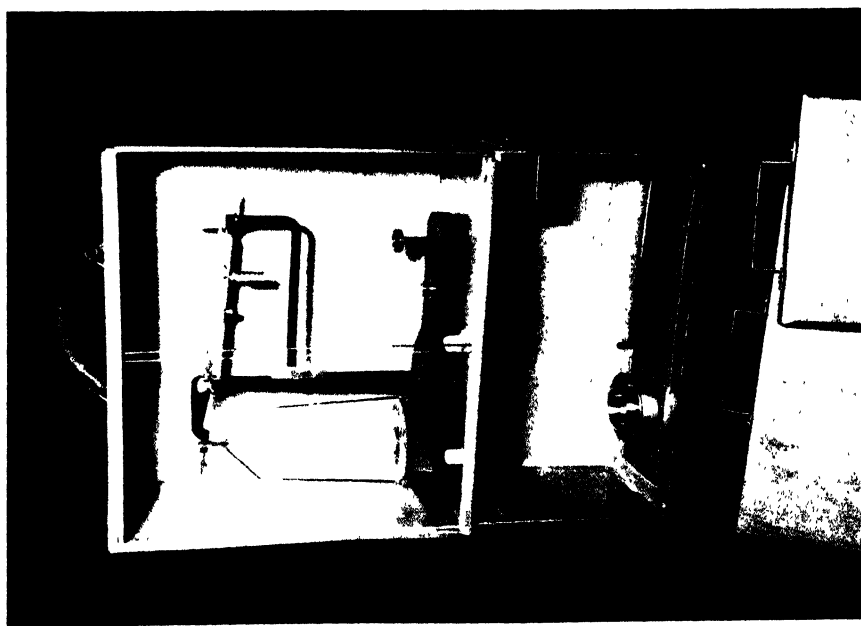


FIG. 1



# HYDROGEN-ION ACTIVITY OF COLLOIDAL ACIDS IN SOILS

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It is well known that acids have a quantity factor as well as an intensity factor. The former is determined by the total hydrogen capable of being replaced by a metal; and the latter, by the number of hydrogen ions present, i.e., the dissociation or activity coefficient of the acid. The direct measurement of hydrogen-ion concentration of soils colorimetrically or electrometrically is a well-known method, but sufficient attention has not so far been paid to the methods of measuring catalytic activity of hydrogen ions in soil colloids. The two best known methods of measuring concentration of hydrogen ions by their catalytic activity are hydrolysis of ethyl acetate and inversion of sucrose. These are dealt with in separate sections of this paper.

## HYDROLYSIS OF ETHYL ACETATE

Parker and Bryan (5) compared the inverting and hydrolyzing power of acid soils with sucrose and with ethyl acetate, respectively, both with suspension and with water extract. They found that hydrolysis of ethyl acetate was greatest in water extract and least in soil suspension; on the other hand, sugar inversion was greatest in soil suspension and least in water extract. They concluded, therefore, that acid silicates catalyze the inversion of cane sugar and not the hydrolysis of ethyl acetate, which is brought about only by a higher concentration of H ions in the mass of the soil solution. These authors considered the possibility of a partial neutralization of the acetic acid by its action on the minerals of the soil but thought it would not account for the extremely small hydrolysis brought about by soil suspensions.

When the large amount of exchangeable bases, even in acid soils, is considered, the possibility is by no means remote that almost the whole of the acid would be used up by the soil when the hydrolysis takes place in the presence of soil suspension. Besides, any small quantity of the acid produced in the first instance would be at once removed from solution and would not be available for hastening the reaction by autocatalysis. All the soils used in this study were made completely base free by exhaustive treatment with 0.05 *N* HCl. Thus all the acetic acid produced by hydrolysis remained in solution, no exchangeable bases being present in soil to react with it.

Before experiments with soils were carried out, it was considered desirable to study the reaction with buffer solutions of known pH value in order to standardize working conditions.

*Hydrolysis of ethyl acetate with buffer solutions*

To 47.5-cc. portions of the various buffer mixtures (KCl-HCl, acetic acid-acetate; B. D. H. Universal) were added 2.5-cc. portions of ethyl acetate. The mixtures were shaken in a mechanical shaker for 24 hours at room temperature. The acid formed was determined by titrating the original and the final solution. The experiment was repeated at 50°C. in a constant temperature water bath. Shaking (occasional) was done by hand during 4 hours. After this the mixture was at once cooled in ice and titrated as before. The buffer solutions were 0.2 *N* initially in both cases. The results are given in table 1 and in figure 1.

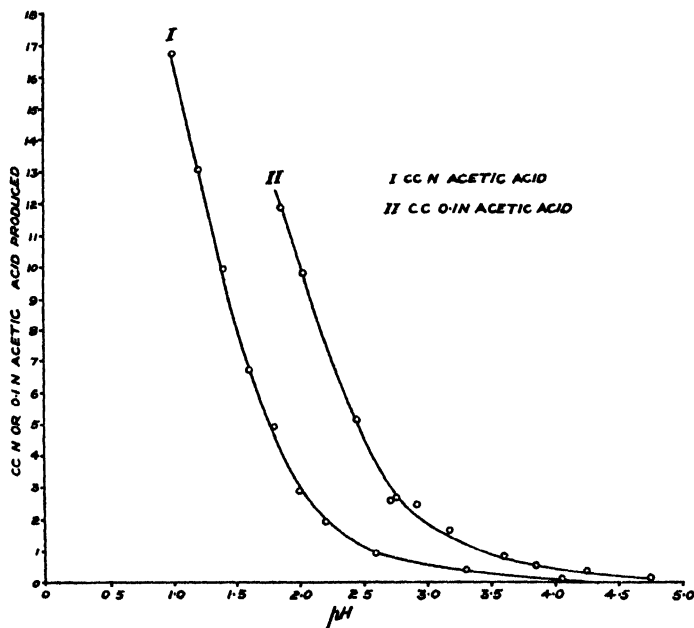


FIG. 1. RELATION BETWEEN pH VALUE AND HYDROLYSIS OF ETHYL ACETATE

It will be seen that the relationship between pH value and hydrolysis of ethyl acetate is capable of being represented by a smooth curve in both cases. It is clear that virtually no hydrolysis occurs above pH 5. If we plot logarithms of the concentration of acetic acid produced against the corresponding pH value, we get straight lines. The relationship is, therefore, capable of being expressed mathematically, and the following formulas are obtained for the two temperatures:

$$\begin{array}{ll} \text{Room temperature, 24 hours' shaking} & \text{pH} = 5 - 1.5 \log_{10} E \\ \text{A } 50^{\circ}\text{C.} & \text{pH} = 4.6 - 1.2 \log_{10} E \end{array}$$

where *E* is the amount of acetic acid produced in milliequivalents in both cases.

*Effect of the concentration of ethyl acetate solution on hydrolysis*

For a study of the effect of the concentration of ethyl acetate solution on hydrolysis, KCl-HCl buffer was used, both the strength of the buffer solution and the concentration of ethyl acetate being varied. The total volume of the buffer and ethyl acetate was 50-cc. in every case. The mixture was kept for 24 hours at room temperature, after which the amount of acetic acid

TABLE 1  
*Hydrolysis of ethyl acetate with buffer of varying pH value*

ROOM TEMPERATURE 24 HOURS		TEMPERATURE 50°C. 4 HOURS	
pH	0.1N acetic acid produced	pH	1 N acetic acid produced
	cc.		cc.
1.86	11.85	1.0	16.725
2.03	9.75	1.2	13.05
2.46	5.10	1.4	9.90
2.59	4.24	1.6	6.70
2.72	2.55	1.8	4.90
2.78	2.62	2.0	2.85
2.93	2.40	2.2	1.90
3.18	1.60	2.59	0.90
3.63	0.80	3.32	0.35
3.87	0.50	4.06	0.05

TABLE 2  
*Effect of concentration of ethyl acetate and buffer solution on hydrolysis*

CONCENTRATION OF BUFFER	pH	CONCENTRATION OF ETHYL ACETATE, PER CENT					
		1	2	4	6	8	10
		0.1 N acetic acid produced					
N		cc.	cc.	cc.	cc.	cc.	cc.
2.0	1.85	4.6	9.5	18.9	28.2	36.2	41.5
1.0	2.03	2.15	4.2	8.10	9.75	15.2	17.8
0.4	2.47	0.82	2.04	4.08	6.02	8.66	9.10
0.2	2.73	0.46	1.02	2.03	3.04	4.05	5.06
0.1	3.07	0.26	0.51	1.02	1.62	2.03	.. .

produced was determined by titrating the original solution and the solution after hydrolysis. The results are given in table 2.

It will be seen from table 2 that the rate of hydrolysis depends on the concentration of ethyl acetate as well as on the concentration of the buffer solution. It must be remembered, however, that the effect of concentration of the buffer is only apparent because dilution affects the pH value of the buffer. The results in tables 1 and 2, if considered on the basis of pH value, are in general agreement. Thus, if we plot logarithms of concentration of acetic acid pro-

duced against pH values, series of straight lines are produced and the relationship can be expressed by the following formulas:

$\text{pH} = 2.5 \log_{10} \frac{C_e}{E}$ , where  $C_e$  is the concentration of ethyl acetate, expressed in cubic centimeters per 100 cc., and  $E$  is the amount of acetic acid produced, expressed in cubic centimeters of 0.1  $N$  solution.

Since  $\text{pH} = \log \frac{1}{C_h}$  where  $C_h$  is concentration of hydrogen ions, we have

$$\log \frac{1}{C_h} \cdot \frac{E}{C_e} = 2.5$$

or

$$\frac{E}{C_e \cdot C_h} = 10^{2.5}, \text{ i.e., } E = C_e \cdot C_h \times 10^{2.5}$$

which follows from the law of mass action, i.e., hydrolysis is proportional to the product of the active masses, which are the hydrogen ions and ethyl acetate in this case.

It might be pointed out that the maximum solubility of ethyl acetate in water is slightly more than 9 per cent; therefore, the values for 8 and 10 per cent solutions are not very different.

#### *Effect of temperature on hydrolysis of ethyl acetate*

A mixture of 47.5 cc. of KCl-HCl buffer of 2.03 pH and 2.5 cc. of ethyl acetate was shaken in a water bath for 1 hour at various temperatures. The results are plotted in figure 2.

It will be seen that temperature plays an important part in the rate of hydrolysis of ethyl-acetate, virtually no hydrolysis occurring at or below a temperature of 10°C.

#### *Hydrolysis with soils*

In order to standardize working conditions a number of experiments were performed with one soil, a black cotton soil of high base exchange capacity. It was treated exhaustively with 0.05  $N$  HCl to remove all the exchangeable bases and to convert the clay complex into the acidoid state, followed by leaching with water until the filtrate was free of Cl ions. Two samples, designated P.C. 2 and P.C. 13, from different localities were treated.

The following experiments were carried out with these soils to study the effect of various factors.

#### *Effect of time of contact and the quantity of soil on the hydrolysis of ethyl acetate.*

Varying amounts of P.C. 2 soil were shaken with 100-cc. of 5 per cent (by volume) solution of ethyl acetate for different lengths of time, after which the suspensions were filtered, and 50-cc. of the filtrate was titrated against standard NaOH, phenolphthalein being used as indicator. The experiment was repeated both at room temperature (23°C.) with 24 hours' shaking, and at 50°C. with 4 hours' shaking. The results are plotted in figure 3, from which it will be seen that the hydrolysis is directly proportional to the amount of

soil. There is a faint indication that the relationship may be exponential, but it is also possible that a very large amount of soil might interfere with the free movement of ethyl acetate, and a slight falling off of the rate of hydrolysis might be expected. It is interesting to note that the pH value of the same soil was determined by the quinhydrone electrode by using soil-water ratios ranging from 1:10 to 7:10. There was absolutely no difference in the pH value, which remained constant at 3.80 irrespective of the soil-water ratio. We have already seen that the change in the rate of hydrolysis in KCl-HCl buffers due to change in concentration of the buffer is entirely ac-

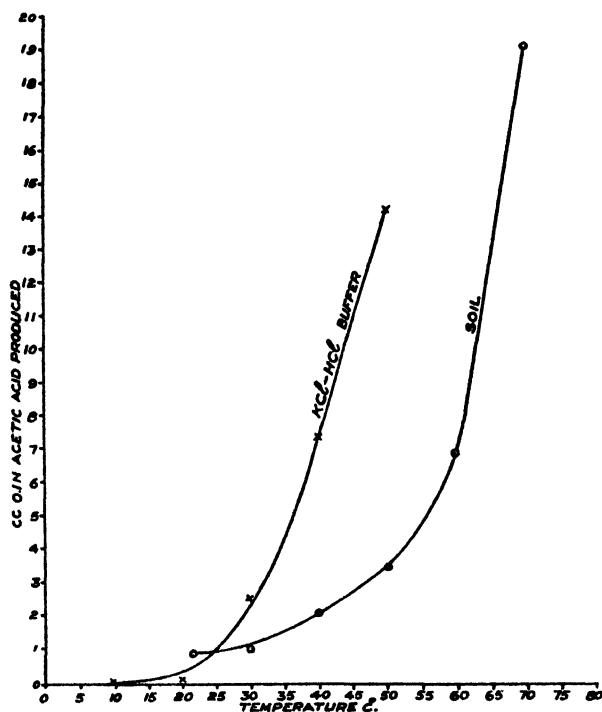


FIG. 2. EFFECT OF TEMPERATURE ON HYDROLYSIS OF ETHYL ACETATE BY SOIL AND KCl-HCl BUFFER AT pH 2.03

counted for by the change in the pH value of the buffer due to dilution (table 2). It is, therefore, evident that the usual electrometric methods of measuring pH values do not give the correct pH value of an acidoid. This conclusion is not surprising when we remember that acidoids are ionized only on the surface and that no hydrogen ions are in true solution.

*Effect of concentration of ethyl acetate on its hydrolysis by soil.* Fifty cubic centimeters of mixtures of ethyl acetate and water in varying proportions were stirred with different amounts of soil for 4 hours at 50°C., after which they were at once cooled in ice, filtered, and titrated. The results are plotted



in figure 4. It will be seen that hydrolysis is directly proportional to the concentration of ethyl acetate. This conclusion was also reached in the case of buffer solutions.

*Effect of temperature on hydrolysis by soils.* Ten-gram portions of P.C. 2 soil were shaken for 1 hour with 100-cc. of 5 per cent ethyl acetate solution at different temperatures, and the hydrolysis was measured as usual by titrating the acetic acid in the filtrate. The results are included in figure 2. The results with KCl-HCl buffer of 2.03 pH, in the same graph (fig. 2), indicate

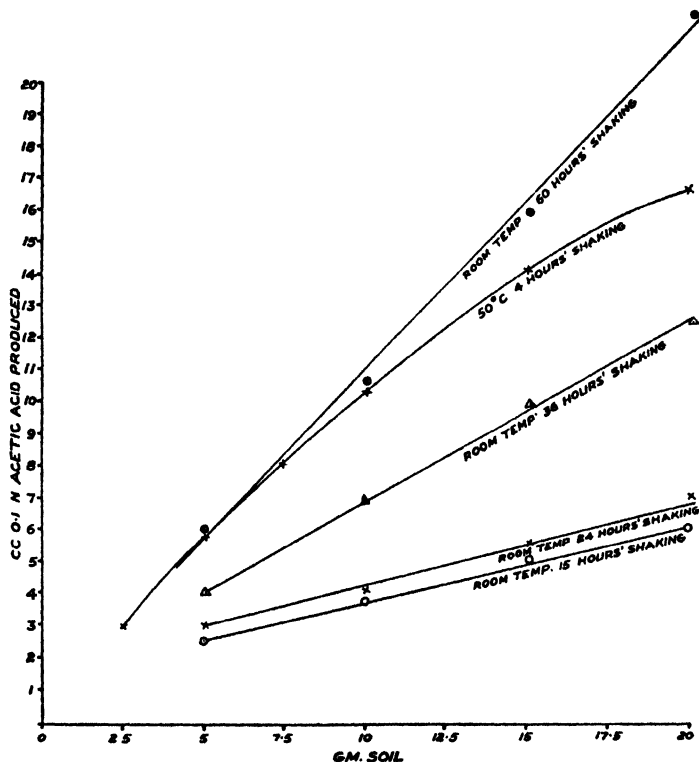


FIG. 3. EFFECT OF TIME OF SHAKING AND OF QUANTITY OF SOIL ON THE HYDROLYSIS OF ETHYL ACETATE

that the hydrolysis by the buffer solution shows a sudden rise at 25°C., whereas in the hydrolysis by soil, this rise takes place at about 50°C. This is to be expected, as the pH value of the buffer is 2.03 and that of the soil is 3.80. The general shape of both curves, however, is similar and leaves no doubt as to the essential analogy between colloidal acids and true acids.

*Hydrolysis of ethyl acetate in alcoholic solutions.* Very few measurements of the pH values of alcoholic solutions have been attempted. Alcohol, however, is well known to suppress the ionization of electrolytes. A similar

effect on the surface ionization of acidoids would be expected. This would result in decreased hydrogen-ion activity and consequently in a diminished rate of hydrolysis. Ten-gram portions of P.C. 2 soil were shaken with 50-cc. of 5 per cent alcoholic solutions of ethyl acetate containing varying amounts of alcohol. The results are given in table 3. It will be seen that alcohol decreases the hydrolysis to a marked extent. This is in agreement with its known effect on other electrolytes, in suppressing their dissociation. The dissociation of acidoids, therefore, is of the same type as the dissociation of true electrolytes.

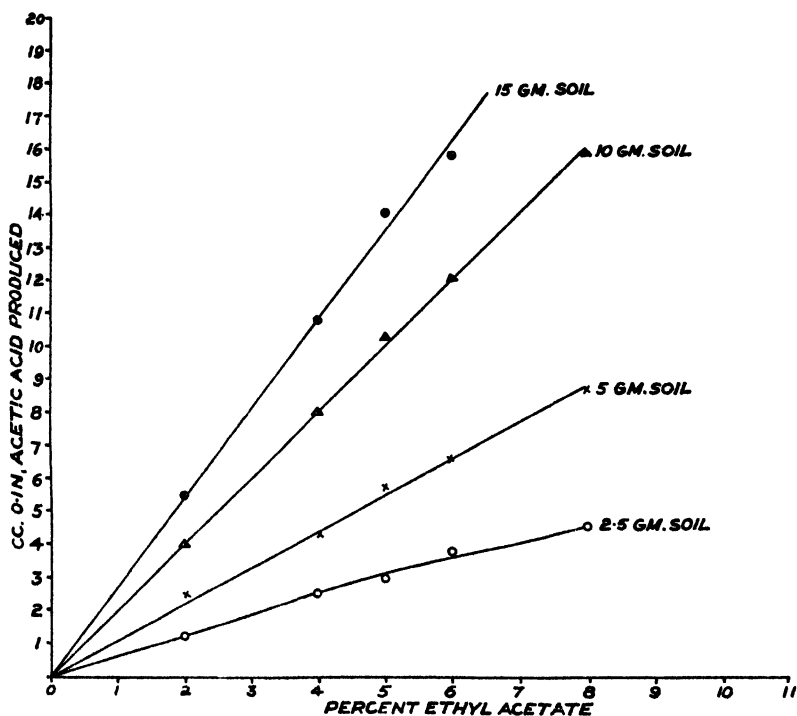


FIG. 4. EFFECT OF CONCENTRATION OF ETHYL ACETATE ON HYDROLYSIS BY SOIL

*Effect of gradual neutralization of the soil acidoid on the hydrolysis of ethyl acetate.* P.C. 13 soil was neutralized with NaOH by the addition of increasing amounts of the alkali to 10-gm. portions of soil. Sufficient water and ethyl acetate were added to give 50-cc. of 5 per cent solution in every case. The mixtures were kept at 50°C. for 4 hours with frequent shaking by hand. After this, they were cooled and filtered, and an aliquot of the filtrate was titrated as usual to determine the acetic acid formed. The results are given in table 4. It will be seen that the first lot of alkali produces a great change in the hydrolyzing power, after which the change becomes more gradual until the

hydrolyzing power is completely destroyed. Because of the limited range for soils in which hydrolysis is possible, as hydrolysis ceases altogether at pH values above 5.35, the method is not suitable for finding the titration curves of soils. The results are interesting, however, in establishing the analogy between acidoids and true acids.

#### HYDROLYSIS OF ETHYL ACETATE WITH DIFFERENT SOILS

The working conditions having been standardized, it appeared of interest to determine the pH value of acidoids from different soils. Forty-two soils from different places were examined in this connection.<sup>1</sup> They were treated

TABLE 3  
*Hydrolysis of ethyl acetate in alcoholic solutions*

ALCOHOL	0.1 N ACETIC ACID PRODUCED
<i>per cent</i>	<i>cc.</i>
0	4.25
85	1.6
90	1.5
95	1.4
100 (absolute)	0.9

TABLE 4  
*Hydrolysis of ethyl acetate by P.C. 13 soil gradually neutralized with NaOH*

0.1 N NaOH ADDED TO 10 GM. OF SOIL	pH	0.1 N ACETIC ACID PRODUCED IN 50 CC.
<i>cc.</i>		<i>cc.</i>
0	3.49	10.25
10	4.45	5.00
20	4.85	3.50
30	5.35	2.00
40	6.25	0.0
50	7.50	0.0

first with 0.05 N HCl until free from exchangeable bases and then with water until free from Cl ions. A final washing with alcohol was given to facilitate drying and powdering.

Ten-gram portions of the treated soil were shaken with 50-cc. of 5 per cent ethyl acetate solution for 4 hours at 50°C. Shaking was done by hand at frequent intervals, after which the mixture was cooled and filtrated, and an aliquot was titrated with standard alkali. From the quantity of acetic acid produced, the pH value was interpolated from figure 1. The pH value of the original soil as well as the pH values of the treated soils were determined

<sup>1</sup>These soils were from Professor Mitscherlich's collection which he had used for experiments on manurial requirements.

TABLE 5

*Inversion of sucrose and hydrolysis of ethyl acetate by various soils, together with other constants*

SERIAL NUMBER	CLAY	pH OF ORIG- INAL SOIL	pH OF ACID-TREATED SOIL			DISPLACED ACID BY KCL, PER 100 GM. SOIL				TITRA- TION TO pH 5, ALKALI PER 100 GM. SOIL	HYDROLY- SIS, ACID	SUGAR INVER- SION
			Direct	Hy- droly- sis	Sugar inver- sion	Single treat- ment		Leaching				
						Phenol- phthal- ein	Methyl orange	Phenol- phthal- ein	Methyl orange			
	per cent					m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	gm.
1	32.2	7.32	3.18	3.24	3.28	12.0	4.0	15.5	5.3	15.0	0.4	0.5048
2	13.8	7.49	3.77	3.75	.	6.0	0.8	8.0	1.5	3.75	0.15	.
3	20.6	7.64	3.67	3.80	3.96	5.6	0.8	8.9	2.0	5.0	0.125	0.0850
4	8.7	7.64	3.67	3.75	4.06	4.0	0.8	6.7	1.3	3.75	0.15	0.1050
5	11.5	7.92	3.67	3.55	3.52	8.8	2.4	11.6	3.0	4.5	0.225	0.225
6	16.0	8.14	4.29	3.80	3.82	4.0	.	6.3	0.2	2.0	0.125	0.120
7	13.9	7.90	3.57	3.68	3.54	5.6	1.2	8.2	2.0	5.5	0.175	0.200
8	29.8	7.50	3.08	3.22	3.28	11.6	4.4	13.5	4.1	12.0	0.41	0.4875
9	9.3	7.61	3.42	3.68	4.02	5.2	0.4	7.0	1.1	3.5	0.175	0.075
10	25.3	6.94	3.44	3.22	3.42	10.0	2.6	11.4	2.2	10.2	0.325	0.325
11	19.1	7.52	3.80	3.68	3.58	5.84	1.2	9.32	1.9	2.37	0.175	0.195
12	18.3	6.84	3.31	3.55	3.52	6.56	2.0	6.7	3.2	2.90	0.225	0.230
13	9.0	7.30	4.23	4.02	4.23	2.8	.	4.9	0.2	0.5	0.6	0.0475
14	15.8	7.56	3.38	3.58	3.66	6.0	1.6	6.5	2.8	1.62	0.2125	0.165
15	25.7	7.74	3.38	3.40	3.45	9.2	3.2	11.0	3.0	4.5	0.3	0.287
16	5.8	7.78	3.77	3.80	3.91	3.6	0.4	5.5	1.0	0.89	0.125	0.95
17	14.6	6.68	3.98	3.88	4.00	3.2	...	5.6	0.6	1.12	0.100	0.80
18	33.3	5.60	3.84	3.80	3.72	4.8	1.2	6.8	1.3	1.62	0.125	0.145
19	27.8	5.92	3.83	3.75	3.64	6.8	1.6	9.2	2.1	2.12	0.15	0.175
20	20.7	7.54	4.07	3.95	3.94	3.6	.	5.2	0.1	1.0	0.075	0.090
21	8.9	7.76	.	.	.	7.1	3.8	10.2	5.1	.	0.633	0.300
22	2.3	7.84	3.54	3.75	3.78	3.4	1.0	5.3	1.6	1.62	0.15	0.130
23	16.4	7.98	3.77	3.88	3.72	4.8	1.4	6.3	1.7	1.25	0.10	0.146
24	8.9	7.51	4.06	3.95	4.00	3.2	0.2	4.1	0.3	0.75	0.075	0.080
25	15.4	8.00	3.44	3.50	3.57	6.2	2.0	7.4	2.6	3.25	0.25	0.200
26	19.6	7.70	3.44	3.70	5.58	5.6	1.6	7.2	2.3	2.12	0.165	0.195
28	11.9	7.16	4.23	3.95	4.06	3.4	0.4	4.7	0.6	0.89	0.075	0.070
29	10.9	7.66	4.13	3.54	3.90	4.0	0.4	5.1	0.7	1.12	0.238	0.10
30	18.8	6.96	3.42	3.75	3.90	5.8	2.0	7.2	2.4	1.89	0.15	0.10
31	8.3	6.52	3.87	4.04	4.10	2.4	0	3.3	0	0.75	0.05	0.065
32	22.9	6.96	3.38	3.68	3.38	7.2	2.6	9.4	3.3	2.89	0.175	0.37
33	16.0	7.64	4.10	3.95	3.80	3.2	0.8	5.0	1.3	0.75	0.075	0.12
34	6.9	5.08	4.49	4.06	4.18	2.6	0.6	4.3	0.7	0.5	0.15	0.055
35	22.8	5.23	3.67	3.75	3.78	5.0	1.6	6.5	1.7	1.5	0.15	0.130
36	5.4	5.18	4.49	4.0	4.30	2.4	0.2	3.4	0.3	0.5	0.0625	0.040
37	8.0	6.62	3.20	3.62	3.57	4.0	1.2	5.5	1.6	2.12	0.188	0.225
38	9.6	7.56	3.80	3.80	3.60	3.8	1.0	5.4	1.2	0.89	0.125	0.185
39	12.8	7.12	3.41	3.80	3.54	3.6	0.8	4.9	1.0	1.25	0.125	0.215
40	47.0	5.16	3.64	3.80	3.59	3.0	0.6	5.7	1.3	3.75	0.125	0.190
41	48.3	5.76	4.58	3.82	3.78	4.0	0.4	5.8	0.8	0.75	0.125	0.130
42	19.1	5.68	3.74	3.80	3.50	6.2	2.0	7.9	2.3	1.5	0.125	0.235
P.C. 1	11.3	8.48	4.26	3.62	3.92	3.2	0.4	4.4	0.4	0.45	0.2	0.095
P.C. 2	59.3	8.23	3.84	3.40	...	35.2	5.0	36.9	5.6	5.5	0.3	0.700
P.C. 3	62.2	7.56	3.25	2.62	...	28.6	4.0	31.1	4.3	19.5	0.85	0.950
P.C. 7	21.8	9.59	5.31	4.22	4.36	2.2	0.2	3.1	0.3	0.0	0.25	0.035
P.C. 13	58.9	8.57	3.49	2.60	...	27.8	10.0	31.1	12.5	12.2	0.025	1.5169
P.C. 15	22.4	7.85	4.66	4.06	4.10	2.8	0.4	3.9	0.4	0.2	0.05	0.065
						$S_p$	$S_m$	$L_p$	$L_m$	$T$	$H$	$I$

with the quinhydrone electrode. The treated soils were also shaken with *N* KCl solution, and the total acid produced in a single shaking, as well as after leaching with KCl, was also determined. The results are given in table 5.

It will be seen that the agreement between the pH values determined directly and those found by hydrolysis is good. When the inherent errors in the measurement of pH value of soils by the electrical as well as by the hydrolysis method are considered, the agreement must be reckoned as very close.

The titration curves of the treated soils were determined with the quinhydrone electrode, NaOH being used to neutralize the soils. The object was to see whether there was any correlation between the amount of alkali required to bring the soil to pH 5 and its hydrolyzing power. A good correlation was expected, as all hydrolysis ceases at pH 5. One gram of soil was left for 24 hours in 5 cc. of NaOH solution of increasing concentration. The pH values were then determined with the quinhydrone electrode. From the titration curves thus obtained the alkali required to bring the soil to pH 5 was interpolated. These interpolated values are included in table 5. It is well known that neutral salts, on coming into contact with acidoids, bring into solution true acids, together with some aluminum and iron. Opinion differs as to the mechanism of this aluminum dissolution. Some regard it as the result of replacement from the soil; others consider it a produce of secondary reactions between the acid produced and the clay complex. Al and Fe brought into solution behave like acids. They are, however, distinguished from the true acids by titration with alkali, methyl orange being used as indicator. If the titrations are conducted in the presence of phenolphthalein, Al and Fe appear as acid. It was of interest to determine the relation between the acid produced by the replacement with a neutral salt and the hydrolyzing power of the soil. Ten-gram portions of the acid-treated soils were taken with 200 cc. *N* KCl solution for 2 hours and filtered. An aliquot of the filtrate was titrated with standard alkali, phenolphthalein being used as indicator. Another aliquot was titrated with the same alkali, methyl orange being used as indicator. The soil was then leached with 500 cc. *N* KCl in 100-cc. lots. The combined filtrates were made up to a definite volume, and aliquotes were titrated to phenolphthalein as well as to methyl orange. The results are included in table 5.

The following correlations were worked out between hydrolysis in milliequivalents of acid produced (*H*) and (*S<sub>p</sub>*) displaced acid with KCl single treatment, titrations to phenolphthalein; (*S<sub>m</sub>*) same as (*S<sub>p</sub>*) but titrations to methyl orange; (*L<sub>p</sub>*) displaced acid by leaching with KCl solution, titrations to phenolphthalein; (*L<sub>m</sub>*) same as (*L<sub>p</sub>*) but titrations to methyl orange; (*T*) titration of soil to pH 5 with NaOH (all quantities expressed in milliequivalents per 100-gm. of soil):

	( <i>S<sub>p</sub></i> )	( <i>S<sub>m</sub></i> )	( <i>L<sub>p</sub></i> )	( <i>L<sub>m</sub></i> )	( <i>T</i> )
( <i>H</i> ).....	0.69	0.77	0.59	0.77	0.82

It will be seen that correlation is best between  $T$  and  $H$ , that is, titration value to pH 5 and the hydrolysis of ethyl acetate. The correlation between  $H$  and displaced acid is better when titration is done with methyl orange than with phenolphthalein. This will be readily understood from the fact that both hydrolysis and inversion become inappreciable above pH 5. The acid displaced above this pH value, therefore, will not be correlated. It must be pointed out that a correlation between intensity and capacity is not strictly justified, because we know that pH and exchangeable bases cannot be correlated; however, in the case of completely unsaturated soils a correlation between quantity and intensity might be expected, provided the dissociation constants of colloidal acids in different soils were close to one another. The validity of this assumption is confirmed by the significance of the correlation.

#### SUGAR INVERSION

Inversion of sucrose by soil has been studied by Hanley (3) and more critically by Rice and Osugi (7), who showed that a suspension of soil inverts several times as much sugar as does an extract of the same soil. The experimental technic employed by these workers left much to be desired. This was pointed out by the senior author in an earlier publication (6), in which some preliminary results were given.

In ordinary circumstances, with mineral acids, the polarimetric method of determining inversion of sucrose is the best. Difficulties are experienced, however, in the use of the polarimetric method with soils: first, it is difficult to obtain a clear solution in many cases; secondly, the actual inversion is very small as compared to the total concentration of the sugar solution, and consequently only a very small change occurs in the polarimetric reading, which is already very high. Titration of Fehling solution was free from these objections and was successfully used in this case.

Standard Fehling solutions were made (a) by dissolving 69.28 gm. of  $\text{CuSO}_4(\text{A.R.})$  to 1 liter, (b) by dissolving 350 gm. of Rochelle salt (sodium potassium tartrate) and 120 gm. of pure  $\text{NaOH}$  and making up to 1 liter. Five cubic centimeters each of the two solutions were mixed, diluted with about 30-cc. of water, and gently boiled. The boiling solution was titrated with the sugar solution, care being taken that the glucose in the solution did not exceed 1 per cent. Near the end point, which was determined by a preliminary rough titration, two drops of 10 per cent methylene blue were added. Every time the Fehling solution was used, it was standardized with freshly prepared 1 per cent glucose solution.

As both glucose and fructose formed by inversion, better known as invert sugar, are capable of reducing Fehling solution, it was always the total invert sugar solution that was determined. A blank reading with sugar solution used was also taken every time to allow for the glucose in it.

*Relation between pH value and sugar inversion*

Acetate-acetic acid buffers of different pH values were used in the study of the relation between pH value and sugar inversion. The results are plotted in figure 5. It will be seen that the general shape of the curve is similar to that expressing the hydrolysis of ethyl acetate in terms of pH value, and the relation is defined by the following formula:

$$\text{pH} = 2.3 - \log_{10} E$$

when  $E$  is the sugar inversion in grams per 25-cc.

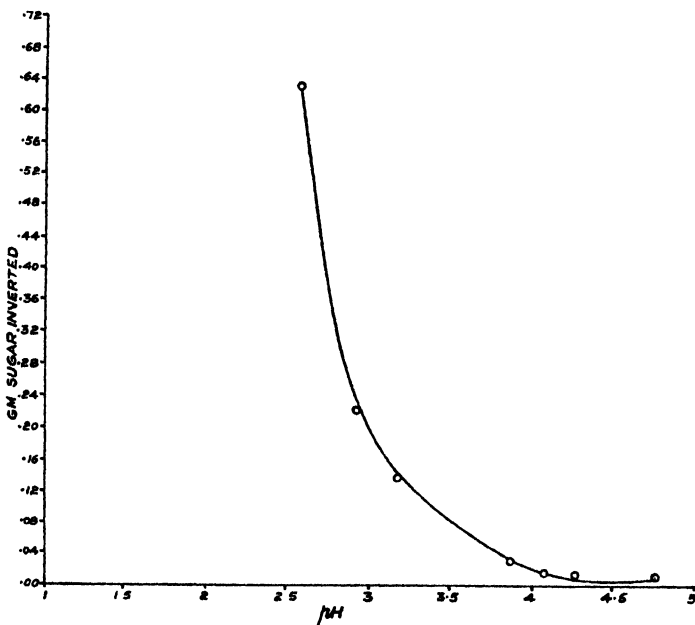


FIG. 5. RELATION BETWEEN pH VALUES AND SUGAR INVERSION Na-ACETATE-ACETIC ACID BUFFER, 4 HOURS' SHAKING AT 60°C.

*Effect of time and concentration of sugar on inversion by soil*

Inversion of sugar was studied by taking 2.5 gm. of P.C. 2 soil and 25-cc. of sugar solution of varying concentration. The mixtures were kept in a water bath at 40°C. for periods of times ranging from 15 minutes to 4 hours. After that the bottles were immediately cooled in ice water and filtered. Ten cubic centimeters of the filtrate was added to 10-cc. of the Fehling solution. Reduction of the Fehling solution was completed with standard glucose solution. The decrease in the quantity of glucose solution from that required for the original Fehling solution was equivalent to the invert sugar in the unknown sugar solution. The inversion was, thus, known in terms of a standard solution of glucose. The results are given in table 6.

It will be seen that inversion of sugar, like the hydrolysis of ethyl acetate, depends on the concentration of sugar and the time of contact.

TABLE 6

*Effect of time and concentration of sugar on its inversion by soil (P.C. 2)*

TIME OF CONTACT	INVERT SUGAR IN 25 CC. AT VARIOUS CONCENTRATIONS OF SUGAR SOLUTION				
	2 per cent	8 per cent	12 per cent	16 per cent	20 per cent
hours	gm.	gm.	gm.	gm.	gm.
0.25	0.0075	0.01	0.01125	0.0175	0.015
0.5	0.01	.	0.01875	0.0200	0.0225
1.0	0.015	0.0225	0.02625	0.0275	0.0325
2.0	0.0175	0.0275	0.03375	0.035	0.0425
3.0	0.0175	0.235	0.04125	0.050	0.055
4.0	0.020	0.040	0.04625	0.60	0.065
5.0	0.020				.. . .

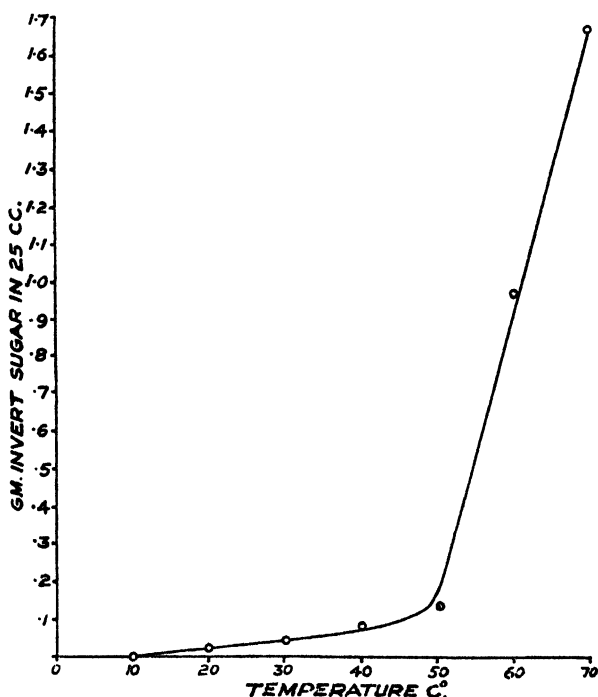


FIG. 6. EFFECT OF TEMPERATURE ON INVERSION BY P.C. 13 SOIL

#### *Effect of temperature on inversion*

To 2.5-gm. portions of P. C. 13 soil in bottles was added 25-cc. of 20 per cent sugar solution. The bottles were kept at different temperatures for 4 hours, being shaken occasionally by hand. The results are plotted in figure



6. It is seen that an abrupt rise occurs in the rate of inversion above  $50^{\circ}\text{C}$ . It appears that the rate of inversion is very slow below  $50^{\circ}\text{C}$ . and that to produce measureable effects the temperature should be about  $60^{\circ}\text{C}$ . The necessity of controlling the temperature in this region is also apparent from the steepness of the curve.

#### *Effect of quantity of soil on inversion*

To quantities of P.C. 13 soil, ranging from 1.25-gm. to 15-gm., were added 25-cc. portions of 20 per cent sugar solution. The mixtures were kept at  $60^{\circ}\text{C}$ . for 4 hours, being occasionally stirred by hand, after which they were

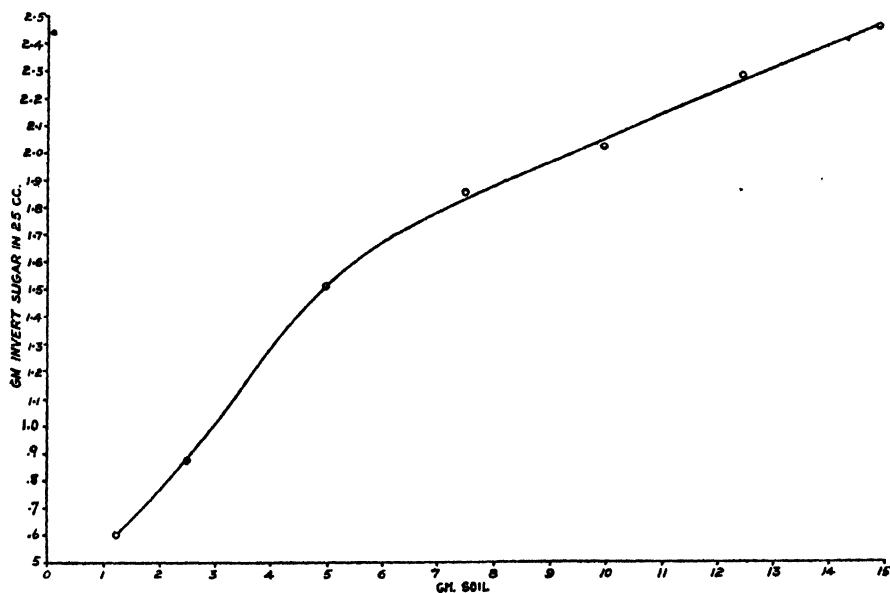


FIG. 7. RELATION BETWEEN QUANTITY OF SOIL AND INVERSION OF SUGAR

cooled in ice and filtered. The filtrate was examined for inversion. The result, plotted in figure 7, show that inversion is proportional to the quantity of soil.

#### *Inversion of sugar with various soils*

The same series of soils used for hydrolysis of ethyl acetate were employed for sugar inversion. Five grams of each soil was kept in contact with 25-cc. of 20 per cent sugar solution at  $60^{\circ}\text{C}$ . for 4 hours.

The pH values of the soils, interpolated from the curve for buffer solutions (fig. 5), were found to be generally lower by 0.6 than those determined by hydrolysis. To obtain pH values of soils comparable with the pH values found by hydrolysis of ethyl acetate, therefore, 0.6 should be added to the

interpolated values. It is a remarkable fact that this lowering of the pH value corresponds with the observations of Moran and Lewis (4) and of Corran and Lewis (1, 2) that sucrose possesses the property of causing a large increase in the activity of various ions while not appreciably altering their concentration. These results are of great importance insofar as they bring the hydron activity of acidoids into line with that of true acids. The results of sugar inversion and the corrected pH values are included in table 5 and show a good agreement with the values obtained by hydrolysis.

Correlation of values for sugar inversion ( $I$ ) with those for displaced acid by KCl, both by single treatment and by leaching, as well as with those for alkali titer to pH 5 were worked out as for hydrolysis of ethyl acetate. The correlation coefficients were as follows:

	( $S_p$ )	( $S_m$ )	( $L_p$ )	( $L_m$ )	( $T$ )
( $I$ ) . . . . .	0.73	0.74	0.62	0.75	0.71

These correlations run parallel to similar correlations worked out for hydrolysis, though they show less variation.

TABLE 7  
*Inversion of sugar with P.C. 13 soil gradually neutralized with NaOH*

0.1 N ALKALI PER 10 GM. OF SOIL	pH	INVERT SUGAR
cc.		gm.
0	3 49	1.542
4	4 05	1.388
10	4.45	1.041
20	4.85	0.625
40	6 25	0 034
60	9 15	....

*Titration curve of soil by sugar inversion*

Five-gram portions of P.C. 13 soil were added to 25-cc. of 20 per cent sugar solution containing different amounts of NaOH. The mixture was kept at 60°C. for 4 hours, and the amount of invert sugar was determined as usual by cooling, filtering, and titrating with Fehling. The results are given in table 7.

A comparison between tables 4 and 7 shows that hydrolysis ceases at a lower pH value than that at which inversion ceases. The shape of the curves showing the relation between pH and hydrolysis as well as the relation between pH and sugar inversion does not admit of extrapolation, but it is clear from those curves that hydrolysis of ethyl acetate becomes inappreciable between 4.5 and 5, whereas inversion stops somewhere about pH 5.5. It is worthy of note that both sugar inversion and hydrolysis continue to take place up to a higher pH value in the case of soils than in the case of buffer solutions. The fact emphasizes the unreliability of the usual electrical methods of measuring soil reaction.

## SUMMARY

Hydrolysis of ethyl acetate and inversion of sucrose were studied with soil acidoids. The general analogy between colloidal acid (acidoids) and true acids has been brought out by a comparison of the catalytic activity of hydrogen ions in both cases.

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# ON THE FORMATION OF STRUCTURE IN SOIL: IV. THE STRUCTURE OF MIXED CLAY-SAND AND CLAY-HUMUS FORMATIONS

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Numerous studies, based on ideas advanced by Gedroiz, regarded the formation of soil structure as a process of simple coagulation of soil colloids under the action of calcium. These studies did not take sufficiently into account the physical conditions of structure formation and the possibility of an orientation of primary elements in the formation of the structural aggregate. Many phenomena of some importance to the understanding of the properties of soil remained unexplained. Examples may be cited which raise doubt as to the correctness of the value attributed to the rôle of absorbed calcium in the formation of watertight structure (1, 8, 11, 15, 21). On the other hand, instances are well known of the failure of a great amount of organic matter, even in the form of slightly soluble calcium humate or aluminum and iron humates, to give rise to a watertight structure in soil (6, 21). To explain these phenomena it proved necessary to resort to various hypotheses, such as that structure formation "is mainly due to humine substances, freshly precipitated under the action of calcium" (25), or that that part of organic matter in soil which is comparatively inert, both biologically and biochemically, is the factor of structure formation (14). To the same class of but weakly grounded hypotheses belongs also that of "active humus" (17). "Active humus" is anything but active in the formation of a watertight structure. The works of Heltzer (8) have established the fact that a watertight structure is formed by an insignificant quantity of organic substance, arising in soil as the result of the process of humus mineralization. Thus we are brought to the necessity of revising our ideas of soil, and our first step in this direction must consist in studying the interactions of the components of soil.

## ON THE NATURE OF MIXED FORMATIONS

There is no need to enumerate the older investigations on the solvent action of humus substances on various minerals and rocks. It need only be remarked that these studies produced no generalizations capable of practical application. Certain individual observations, however, are of interest. They produce evidence that mineral-humus compounds of a continuously changing composition are actually forming. Such compounds were termed "mutable" (3), but, unfortunately, their nature was not explained.

At the present time, with the development of colloid-chemical ideas in their application to soil science, soil colloids are considered as salts of the silicic and humine acids with strong bases or with iron and aluminum hydrates (9). But, as has been noted, neither calcium humates nor humates of trivalent metals produce a watertight granular structure. We must, therefore, turn our attention to phenomena of another, but little investigated, order and seek for explanations of structural properties in the study of the nature of the union of particles of heterogeneous composition and size. The chief observation by which one must be guided in this case, is that the components of soil—sand, clay, humus, oxides—rarely, if ever, are found isolated in soil. The soil-forming process determines the distribution of these components and their mutual orientation. No special studies of this problem have been made. The literature contains only a few references to the possibility of heterogeneous formations, based mainly on the consideration of active colloidal material as an amorphous jellylike mass enveloping solid mineral grains (2, 6). Some authors have thought that these colloidal envelopes lend the soil a cell structure (6, 7). Still earlier, however, Schloesing (13), on the basis of his observations, pointed out the specific rôle of the components of soil in the process of structure formation. He attached great importance to such complexes as clay-sand and clay-humus, in the belief that clay cements sand and that humus cements clay. The author has taken these works of Schloesing as the starting point for further investigations on soil structure.

In his preceding report (15), the author established the existence of a very firm bond between clay and quartz sand. This phenomenon was explained on the basis of the fact that the mixture of clay with sand is subject to the law of mutual orientation based on the similarity of crystalline periods. Besides this kind of bond, an interaction of another order exists between particles of clay and sand. Observation shows that in this case a laminated system is formed, possessing anisotropic properties only when the amount of sand is below a certain limit. Only under such a condition is a structure formed whereby groups of parallel anisotropic clay particles serve as centers of crystallization. Under the microscope one can see the grains of sand uniting with these parallel laminae of clay. The resulting structure of the mixture does not differ from the structure of pure clay. If the amount of sand in the mixture is increased, however, structure disappears, and a clear-cut separation appears between the two components of the mixture.

The phenomenon described can be readily observed under the microscope if the preparation is made as follows: A small quantity of swollen Na-clay gel is placed on a glass slide, and on one side at the very edge of the preparation a little fine quartz sand (0.01–0.02 mm.) is added. If a cover slip is cautiously placed on this preparation, a mixture is obtained in which the concentration of sand gradually decreases toward the opposite edge of the preparation. It is possible to observe under the microscope how the structure disappears in the mixture with a higher content of sand (pl. 4, fig. 1, lower part) and how,

as the sand content decreases, the grains of sand begin to unite with the clay particles, until, at a certain ratio of sand to clay, the structure of the mixture is similar to that of clay (pl. 4, fig. 1, upper part).

The phenomena of structure formation in mixtures of clay and sand, as described, explain the weakening and disappearance of the granular structure in chernozem when this soil is mixed with sand. Such a gradual weakening of structure under the influence of the admixture of sand was observed by Nabokikh in the southern steppes of Ukraine, lying close to the sand dunes of the left banks of steppe rivers (12).

The question of the bond between humus and clay is of no less interest than that of the bond between sand and clay. It is to be expected that the elucidation of the nature of these mixed formations will supply information on the origin of the compact granular structure of chernozem, on the process of its formation, and on the symptoms accompanying its destruction. In our preceding work (15) it was found that clay possesses the ability to bind humus irreversibly, but no typical characteristics for the differentiation of mixtures with a higher or lower humus content by means of microscopic examination were found. Dendritic structure, together with the spheruliths of the monaxial crystal, appeared but rarely.

As original material, we used colloidal Na-clays, as in our earlier experiments, and also rocks containing almost pure kaolinite and bentonite. In preparing the mixtures, Na-humate, isolated from peat, and a water-soluble humate, obtained by decomposing manure, were used. Both kinds of humates were thoroughly purified by dialysis. A study of the X-ray spectra of these humates showed the absence of crystalline substances.

The investigation of the mixtures showed that clay and humus mix in any ratio but that no chemical compound seems to be formed. The formation of the mixture, insofar as one may judge from microscopic analysis, takes place in the following manner. Anisotropic colloidal particles of clay act on the isotropic particles of humus in such a way that the latter become anisotropic and assume the state of equilibrium corresponding to their anisotropic condition. Lamina of the clay substance serve as centers of crystallization, and the ability of humus to crystallize is determined by the number of such centers. If the amount of humus does not exceed the number of centers of crystallization, the structure of the mixture seems perfectly homogeneous and makes up an integral mass, differing in no way from the structure of pure clay. Thus, clay is the substance governing crystallization. If the amount of humus exceeds the number of centers of crystallization, the excess humus assumes the state of equilibrium which corresponds to its isotropic condition. A segregation of the mixture, corresponding to the different states of equilibrium, takes place. Isotropic humus, having a high surface tension, must distribute itself on the periphery of the mixed clay-humus formation, and the more viscous crystalline component substance of the mixture will occupy a central position. In liquid mixtures containing a great excess of humus, the state of

equilibrium corresponding to the isotropic condition of humus prevails, as a result of which double refraction disappears.

Evidence that the phenomena described actually take place may be obtained both with the aid of physicochemical methods of studying mixed clay-humus formations and with that of X-ray or microscopic investigation.

Humus, crystallizing on clay, forms a kind of pseudomorphosis and thus is in the closest possible contact with the particles of clay. This contact leads to a lowering of solubility as the result of the compression of the ion envelope around the particles. It is evident, from my observations, described in a preceding report (15), and from the experiments of Tyulin (19, 20), that a relatively large amount of humus is firmly held by clay even when this is subjected to hydrolysis with strong alkali. Another observation, consistent with that of the lowering of the solubility of humus held by clay, is that the absorption capacity of gels containing firmly held organic matter decreases abruptly in comparison with that of the free fraction of humates (20). Other experiments of Tyulin show that the elimination of humus by oxidation with hydrogen peroxide gave rise to an increasing exchange capacity of the clay to which the humus had been firmly held. A similar phenomenon of the increase of exchange capacity after  $H_2O_2$  treatment was observed by Meyers for Hays-colloid, isolated from chernozem (11).

In addition to the mixtures prepared from pure kaolinite or bentonite and humus, samples of gels isolated from soil at the Suma Agricultural Experimental Station by the method of fractional peptization were also subjected to X-ray analysis (16). These gel samples differed in regard to the firmness of their bond with humus, and their clay content ranged from 13.2 to 85.4 per cent. In every case, both in artificially prepared mixtures and in gel samples isolated from soil, the spectra obtained proved to be those of the clay component. This shows that we are dealing here with a nonhomogeneous formation, composed of two homogeneous parts united and mutually oriented in a definite manner. Microscopic study shows that the mixture is composed of clay laminas, surrounded by humus laminas of the same shape as those of clay. The structure of the mixture, therefore, is no different from that of pure clay (pl. 4, fig. 2).

#### THE INFLUENCE OF AN ADMIXTURE OF IRON AND ALUMINUM HYDROXIDES ON THE BINDING OF HUMUS BY CLAY

Anisotropic colloidal particles of clay when covered with the water films are arranged parallel to one another, forming a doubly refracting system. The formation of one crystal from these particles, each of which forms a continuation of the space lattice of the other, is hindered by admixtures. The purer the clay, the thinner are the laminas of these contaminations. Since the usual contaminations of clay are iron and aluminum hydroxides, it becomes necessary to study the influence of these oxides on the binding of humus. As  $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (göthite) and  $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (bayerite) were used for these

experiments, it was necessary, first, to establish whether they are able to form aggregate anisotropic structures and whether they possess an orienting influence on humus. Observation under the microscope shows that neither of these hydroxides forms anisotropic structures. Mixture of these oxides with humus produces a confused coagulation. It is to be expected, therefore, that with the increase of admixed sesquioxides, not only will the inherent ability of clay particles to aggregate be lowered, but the orienting influence of clay on humus particles as well. Indeed, observation shows that an increased quantity of iron in colloidal clay lowers the ability of clay to form a structure and to orient humus.

For use in the study of the influence of oxide admixtures, samples were prepared, the chief component of which was kaolinite. Schneeberg (Saxony) kaolin, which was shown by X-ray analysis to be almost pure kaolinite, was chosen for this study. Kaolin was first saturated with Na ions and then thoroughly purified by dialysis. The following materials were utilized as hydroxides for the preparation of mixtures:

Bayerite— $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , a metastable trihydrate, obtained, by the method of Fricke and Meyring (4), by passing  $\text{CO}_2$  into an alkaline solution of aluminate. The precipitate was washed with distilled water and then thoroughly purified by dialysis. The X-ray spectrum of this hydroxide coincided perfectly with the Weiser and Milligan diagram (23).

$\alpha\text{-Fe}_2\text{O}_3$ —stable iron oxide, of a red-brown color, obtained by slowly heating a 0.33 *M* solution of  $\text{FeCl}_3$  to  $90^\circ\text{C}$ ., washing it subsequently with water and then with dilute ammonium hydroxide. The precipitate thus obtained was purified by dialysis. The X-ray pattern corresponded to that of the oxide  $\alpha\text{-Fe}_2\text{O}_3$  (24).

The clay-hydroxide mixtures were prepared in the following manner. Varying quantities of one or both of the hydroxides were added to a definite amount of kaolinite and thoroughly mixed. After the resultant mixtures had become homogeneous, equal quantities of Na-humate were added to each. After the addition of humus, mixing was again carried out and was continued until the mixture became too dry to allow further mixing. This method was used in order to prevent concentration of the humate at the surface of the material as a result of the high surface tension. The mixture was then air dried, and 5-gm. samples, on the dry basis, were taken. These were treated with water in order to isolate the suspensions. The quantity of the suspension isolated was not determined. After the suspension was precipitated with a 2 per cent solution of KCl and washed with a 1 per cent solution of the same salt, the carbon content was determined. The kaolin remaining after the isolation of the suspension, was thoroughly washed with water, and its carbon content, likewise, was determined. The composition of the oxides admixed to kaolin and the amount of carbon firmly bound to the material of the mixture are shown in table 11. The conclusion that the oxides have a positive influence on the binding of humus is applicable only to the admixture of insignificant



amounts of iron and aluminum oxides. Only in this case do anisotropic clay particles have an orienting influence on both the particles of oxides and those of humus. This influence, however, does not extend above a 1 to 2 per cent content of oxides. Increased contents of oxides cause disorientation, and a phenomenon of the same order is observed as that in mixtures of sand with clay and of clay with humus. The binding of humus, observed in mixtures with a higher oxide content, is explained by the flocculation of humus by hydroxides and not by the orienting influence of kaolin.

Microscopic studies of these mixtures confirm the foregoing conclusion. When the quantity of sesquioxides is increased, the anisotropic colloidal particles of kaolinite lose their ability to distribute themselves in parallel rows. This orienting capacity is preserved, however, when the quantity of oxides is insignificant. Microscopic study has shown that with an excess of sesquioxides,

TABLE 11  
*Composition and carbon content per gram of kaolin-oxide mixtures*

COMPOSITION OF MIXTURE	CARBON	
	In kaolin remaining after isolation of suspension	In suspension isolated from kaolin
	mgm.	mgm.
1. Kaolin . . . . .	1.0	47.9
2. Kaolin + 0.27 per cent $\alpha$ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . . . . .	2.2	61.9
3. Kaolin + 0.67 per cent $\alpha$ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . . . . .	1.43	57.2
4. Kaolin + 7.58 per cent $\alpha$ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . . . . .	11.8	77.1
5. Kaolin + 0.33 per cent $\alpha$ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . . . . . + 0.63 per cent $\alpha$ - $\text{Fe}_2\text{O}_3$ . . . . .	2.49	69.3
6. Kaolin + 0.5 per cent $\alpha$ - $\text{Fe}_2\text{O}_3$ . . . . .	1.83	52.5
7. Kaolin + 1.25 per cent $\alpha$ - $\text{Fe}_2\text{O}_3$ . . . . .	3.01	55.7
8. Kaolin + 10.74 per cent $\alpha$ - $\text{Fe}_2\text{O}_3$ . . . . .	13.6	65.5
9. Kaolin + 21.5 per cent $\alpha$ - $\text{Fe}_2\text{O}_3$ . . . . .	29.05	75.7

a confused flocculation of clay particles occurs and no evidence of the presence of a structure possessing vectorial properties is observed.

On the other hand, the elimination of iron and aluminum oxides from the surface of clay particles increases the ability of these particles to aggregate. A suspension of Na-clay (clay "Toida") was treated with Tamm's reagent (18) in order to eliminate iron oxides. The clay precipitate was washed with a 2 per cent NaOH solution and then with pure water, and, finally, it was purified by dialysis. Microscopic examination of this precipitate showed the beginning of structure formation, as evidenced by rotational movement. This was the so-called "rodlike" ["bâtonnet" of Friedel (5)] structure, modified here and there to a cylindric shape with rounded ends. The "rods" disappear between the Nicol prisms along the longitudinal axis (pl. 4, fig. 3) when they form in a liquid so viscous that they cannot move and unite with one another. The rods are optically homogeneous and show positive double refraction.

The structure of the Na-clay before treatment with Tamm's reagent is shown in plate 4, figure 4. The distinctive features of this structure, which characterize the alterations occurring in clay under the influence of the admixture of iron oxides, are negative double refraction, indicating a reconstruction of the micella, and the beginning of a structure formation bearing a close resemblance to the intermediate type of "conic" and "fanlike" structure of mesomorphous bodies (5).

Sufficiently thin envelopes of iron and aluminum oxides on clay particles possess cementing properties, and their action resembles that of intercrystalline layers between the grains of pure metals. In the absence of these interlayers, nothing would hinder the formation of one crystal from the individual particles. According to the general law, increase of the thickness of this interlayer leads to a decrease of cohesion. The accumulation of oxides at the surfaces of the adjoining particles exceeds the optimal dimension of the film, weakens the ability of the particles to aggregate, and gradually leads to their disaggregation.

#### SUMMARY

The nature of mixed clay-sand and clay-humus formations is explained, and structures are described which show that clay is the structure-forming component of soil.

Admixtures of iron and aluminum oxides to clay hinder the aggregation of clay particles. The presence of oxides in large amounts destroys the orienting properties of clay in respect to humus. In this case, mere coagulation occurs with a confused distribution of particles.

The elimination of iron and aluminum oxides from the surface of clay particles increases the ability of these particles to aggregate. A particular "rod" structure arises, the "rods" being optically homogeneous and possessing positive double refraction.

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#### PLATE 4

##### THE STRUCTURE OF CLAY AND OF CLAY-SAND AND CLAY-HUMUS MIXTURES

FIG. 1. Clay-sand mixture. Polarized light. Magnification  $\times 40$ .

FIG. 2. Clay-humus mixture. Polarized light. Magnification  $\times 53$ .

FIG. 3. Clay "Toida" after treatment with Tamm's reagent. Rodlike structure. Polarized light. Magnification  $\times 40$ .

FIG. 4. Clay "Toida" before treatment with Tamm's reagent. Polarized light. Magnification  $\times 40$ .



FIG. 1



FIG. 2



FIG. 3

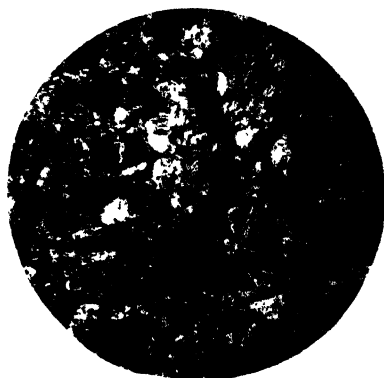


FIG. 4



# MICROBIAL ACTIVITIES IN SOIL: V. MICROBIAL ACTIVITY AND ORGANIC MATTER TRANSFORMATION IN PALOUSE AND HELMER SOILS<sup>1</sup>

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The marked difference in type of microflora in the Palouse and Helmer soils discussed in the preceding paper in this series (23) suggested further studies of the microbial activity in these soils. The particular activity of the microflora and the nature of organic matter transformation resulting from additions of the surface organic residue of one soil to the other, as well as to its homologous soil, and the possible influence these factors may have in differentiating inherent properties of soils developed from the same parent material under similar climatic conditions form the principal objects of the work presented in the present paper.

## EXPERIMENTAL PROCEDURE

Following the removal of the undecomposed organic residues from the surface, a suitable quantity of soil taken to a depth of 10 inches from each of the virgin areas of the Helmer and Palouse soils located near Troy, Idaho, and used for the previous experiment was brought to the laboratory. Duff covering the Helmer soil and litter covering the Palouse soil were also collected. The Helmer soil duff layer, varying from 0.5 to 1.5 inches in thickness, consisted chiefly of twigs and coniferous tree needles in various stages of decomposition. The Palouse soil litter, consisting of a very thin irregularly distributed layer of organic residue, was composed largely of grass vegetation in various stages of decomposition. These residues were air dried and finely ground. The soils were air dried and were then sifted through a 16-mesh sieve to effect thorough mixing and also removal of the coarse organic particles, and determinations were made of the hygroscopic moisture and normal field moisture capacities. The hygroscopic moisture for the Helmer and the Palouse soils was 2.11 and 2.12 per cent respectively, and the normal field moisture capacity was 26 and 25 per cent respectively.

Three 2.5-kgm. samples were taken from the bulk of each soil and placed in brown bottles covered with paper to exclude light and prevent excessive growth of algae and higher plants. Sufficient water was added to the bottles

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to bring the soils to their normal field moisture capacity, which is virtually a static moisture condition with respect to capillary and gravitational movements and is also optimum for plant growth. The bottles were allowed to stand for 4 days to insure uniform distribution of the moisture and to give the microflora a chance to resume normal functioning. The normal field moisture capacity of the soils was maintained within narrow limits throughout the experiment by the addition of water when necessary.

On the fourth day each soil was passed through a 16-mesh sieve several times to insure homogeneity and was treated as follows:

SOIL NUM- BER	SOIL TYPE	TREATMENT	gm.*
1	Helmer silt loam	None	
2	Helmer silt loam	Helmer soil duff (0.578 per cent N)	20.000
		NH <sub>4</sub> NO <sub>3</sub> (34.9 per cent N)	1.387
3	Helmer silt loam	Palouse soil litter (0.703 per cent N)	20.000
		NH <sub>4</sub> NO <sub>3</sub> (34.9 per cent N)	1.316
4	Palouse silt loam	None	
5	Palouse silt loam	Palouse soil litter (0.703 per cent N)	20.000
		NH <sub>4</sub> NO <sub>3</sub> (34.9 per cent N)	1.316
6	Palouse silt loam	Helmer soil duff (0.578 per cent N)	20.000
		NH <sub>4</sub> NO <sub>3</sub> (34.9 per cent N)	1.387

\* Per kilogram of soil.

The finely ground residues reinforced with sufficient ammonium nitrate to make the total nitrogen content equivalent to 3 per cent, thus insuring an ample supply of available nitrogen for maximum microbial activity during the process of organic matter transformation, were mixed thoroughly with the soil at the rate of 2 per cent on the dry soil basis. The mixing was accomplished first by hand and finally by passing several times through a 16-mesh sieve. Samples of soil were then removed for analysis, and the remaining portions, equivalent to 2 kgm. of oven-dried soil, were returned to the bottles, packed by gently tapping the bottles on the table, and connected with an absorption train for CO<sub>2</sub> determination.

The experiment was carried on at room temperatures fluctuating between 18 and 25°C. The numbers of bacteria, actinomyces, fungi, aerobic cellulose-decomposing bacteria, *Azotobacter*, and anaerobic nitrogen-fixing bacteria; CO<sub>2</sub> evolution; oxidation-reduction potentials; and pH values were determined at the beginning and at intervals of 2 or 3 days until maximum microbial counts were obtained. The intervals were then gradually increased to 5, 7, 14, and 30 days.

Chemical analyses were made at intervals for total, nitrate, and ammonia nitrogen as well as for total, hot-water-soluble, sulfuric-acid-soluble, and sulfuric-acid-insoluble carbon and nitrogen. These substances were determined:

A, at the beginning of the experiment; B, 40 days later, when maximum microbial numbers had been obtained; C, at 104 days; and D, at 235 days, when the experiment was terminated. At each sampling time, amounts equivalent to 250 gm. of oven-dried soil were removed, air dried, and stored for subsequent consecutive analysis.

Both the microbial and the chemical analysis were carried out in order to ascertain the relationship between specific groups of microbes and the activity of these groups in influencing the disappearance or accumulation of various chemical components of the soil and, conversely, the effect of these substances in stimulating or inhibiting the development of individual groups of soil microbes. The determination of pH values and of oxidation-reduction potentials was intended as an aid in the interpretation of the results of the microbial activity in the mineralization of organic matter.

At each sampling period the soil from each bottle was passed twice through a 6-mesh sieve to clean paper before the required amount of soil was removed. This treatment was intended to insure thoroughly mixed representative samples and also to prevent the development of anaerobic conditions in the bottles during the course of the experiment. The samples removed for analysis were spread very thinly on clean paper and thus were air dried quickly. The remainder of the soil was returned to the bottles and packed by gentle tapping of the bottles on the table. Water was added when necessary to maintain the moisture content at normal field moisture capacity. The bottles were then reconnected to the CO<sub>2</sub> absorption train.

Immediately after the samples were air dry, 1-gm. portions of soil were used for suitable dilutions of water suspensions for triplicate platings on agar prepared with the proper selective nutrient media for the determination of numbers of bacteria, actinomyces, and fungi. Other suitable portions were spread on triplicate silica gel plates impregnated with the proper nutrient solutions for the determination of numbers of *Azotobacter*, aerobic cellulose-decomposing bacteria, and anaerobic nitrogen-fixing bacteria. The remaining portions of the air-dried samples were used for determinations of pH values and oxidation-reduction potentials. The details of procedure in these methods and in the method for CO<sub>2</sub> determinations are described in a preceding paper in this series (22).

The analyses for total and nitrate nitrogen, and for total and various fractions of organic carbon of the soil samples taken at the A, B, C, and D periods were made also according to the methods described in a preceding paper (23). The ammonia nitrogen was determined by Nesslerization of a 0.01 *N* H<sub>2</sub>SO<sub>4</sub> extract, the acid solution being used to replace any ammonia in the base-exchange complex of the soils.

The method of Waksman and Stevens (29) with the following modifications was used for the fractionation of the organic materials of the soils under investigation. Waksman (25) and others found that fats, resins, and waxes are very resistant to decomposition; hence these fractions were not deter-



mined. Only two extractions—the hot water, and the 72 per cent sulfuric acid—were made. They include the most readily attacked and therefore most important compounds influencing microbial activity.

Inasmuch as the interest in the organic matter transformations in this investigation was focused chiefly on the changes in the organic carbon as affected by microbial activity in the soil, another modification was adopted. The total organic carbon content, instead of reducing sugars, was determined in the extracts as well as in the extracted soil residues and in the unextracted soil. When it is found, for example, that the hot-water-soluble carbon and the sulfuric-acid-soluble carbon in the soil decrease with time, the decreases are explainable only by the fact that a part of the constituents represented by these fractions was destroyed or utilized by the soil microflora. These decreases can be expressed in terms of carbon instead of in terms of sugars, hemicelluloses, or celluloses, as the case may be. It may be objected that the total carbon determinations of hot water or sulfuric acid extracts include carbon from materials other than carbohydrates. Even with these components included, it appears that this method is more suitable for the purpose intended here than is a determination of the reducing sugars in these extracts, for the latter method does not account for certain water-soluble compounds, including starches and dextrines, which are not completely hydrolyzed to reducing sugars, and certain organic acids and other organic compounds which are certainly present in the acid if not in the water extracts. A total carbon determination accounts for all these constituents in terms of carbon and obviates the necessity of using factors in calculating the organic matter content of the soil, factors which, incidently, may vary considerably, according to Waksman and Hutchings (27).

## EXPERIMENTAL RESULTS

### *Carbon dioxide evolution*

The data on  $\text{CO}_2$  production by each soil during the course of the experiment are presented in figures 1 and 2, which indicate a profuse evolution of  $\text{CO}_2$ , particularly from the soils treated with 2 per cent organic residue. The maximum daily  $\text{CO}_2$  production occurred the first day of the experiment, and secondary peaks appeared 10 to 12 days later, suggesting a possible rhythmic variation in the activity of the microflora. Secondary peaks in  $\text{CO}_2$  production have been noted by other investigators. Melin (10) observed them in the decomposition of certain organic residues, but they occurred about 30 days after the initial maximum evolution, which took place during the first two or three days. He explains the first peak on the basis of rapid decomposition of the readily available water-soluble constituents and the second by assuming a more active decomposition of the less decomposable constituents such as celluloses and hemicelluloses. Johannson (8), who obtained similar results, attributes the fluctuations in  $\text{CO}_2$  production to rhythmic variations in microbial activity, on the assumption that periodic fluctuations occur in

the rate of metabolism and the growth velocity of soil microbes. Smith et al. (16) noted that after the initial maximum production of  $\text{CO}_2$  had taken place in soils kept in the laboratory at optimum moisture and temperature conditions, a rather definite rhythmic periodicity in evolution of  $\text{CO}_2$  occurred, but they did not correlate this periodicity with microbial activity as determined by numbers of organisms. Although they concede the possibility

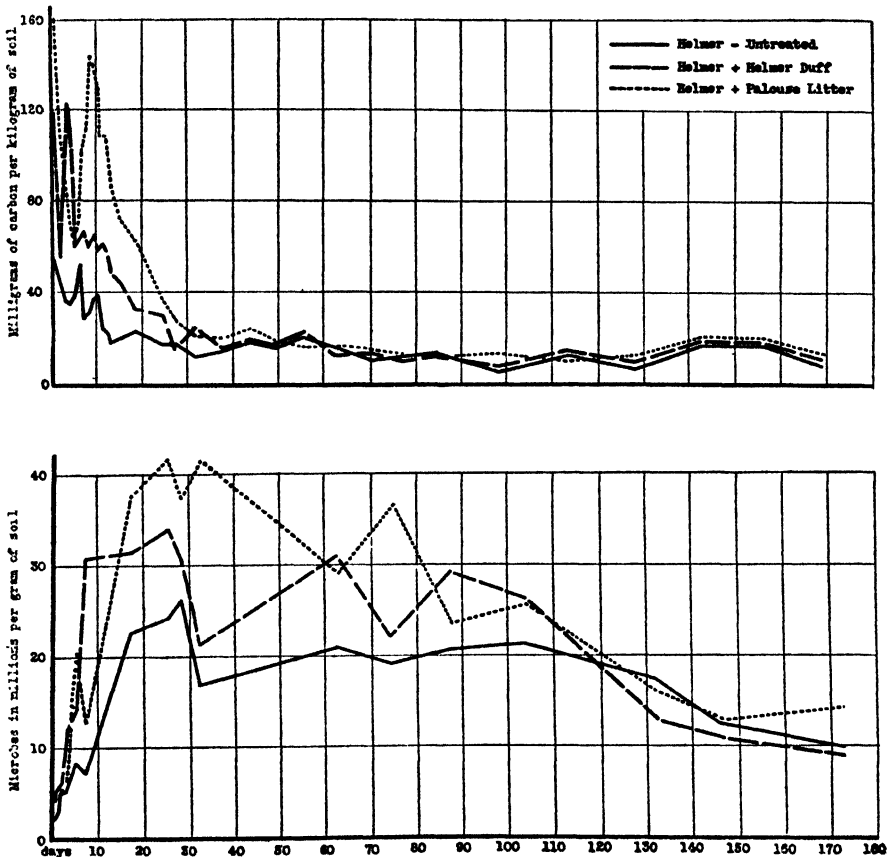


FIG. 1. CARBON DIOXIDE PRODUCTION AND NUMBER OF MICROBES IN VARIOUSLY TREATED HELMER SILT LOAM

of periodic variations in the rate of respiration between the logarithmic growth and logarithmic death phases of microbes, they consider it difficult to conceive that the generation time and the metabolic processes of a mixed culture of microbes which constitutes the soil microflora are sufficiently similar to produce regular periodic fluctuations in the rate of  $\text{CO}_2$  production.

No correlaton was evident between the irregular fluctuations in  $\text{CO}_2$  evolution from the variously treated Helmer and Palouse soils and the microbial

activity as indicated by the numbers of organisms present at the time when these fluctuations were most apparent. Furthermore, a comparison of the data in figures 1 and 2, which present graphically both the amounts of  $\text{CO}_2$  produced and the numbers of microbes present in these soils at various periods of sampling, discloses that the maximum numbers of organisms did not appear until some time after a sharp decline in  $\text{CO}_2$  evolution had taken place. A

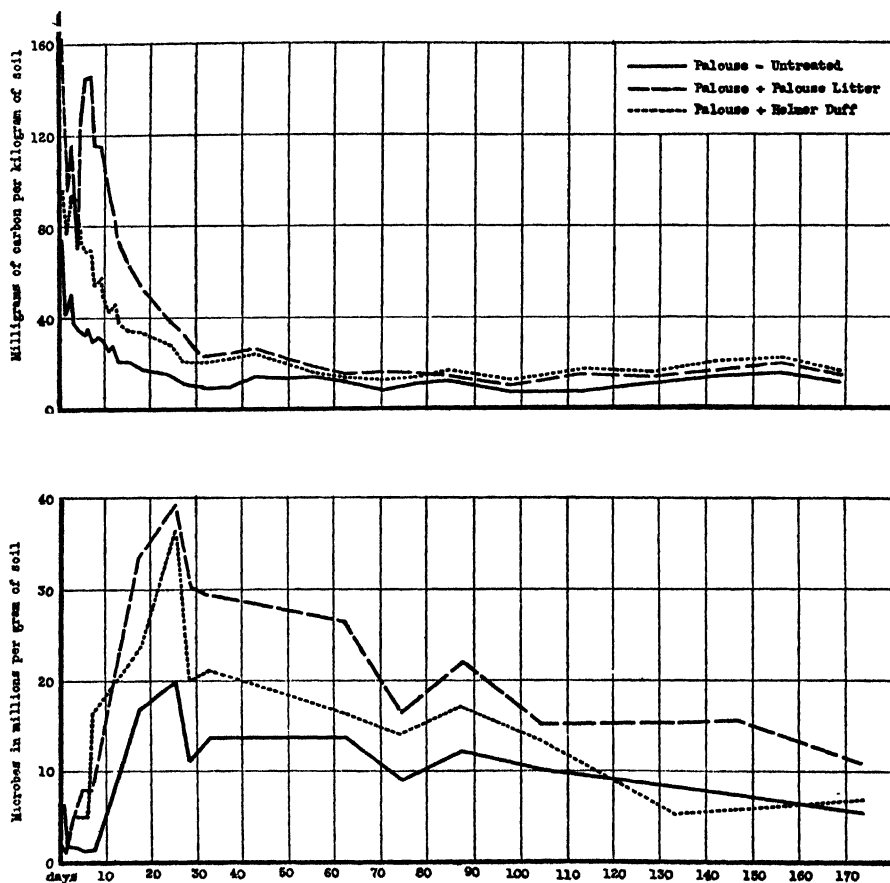


FIG. 2. CARBON DIOXIDE PRODUCTION AND NUMBER OF MICROBES IN VARIOUSLY TREATED PALOUSE SILT LOAM

sharp reduction in  $\text{CO}_2$  production generally occurred at or before the tenth day of the experiment, and this was followed by a more gradual decline, until after 30 days a low but fairly uniform production resulted. The maximum numbers of microbes did not appear until 25 to 30 days had passed. That there is a definite lag between maximum  $\text{CO}_2$  production and maximum numbers of microbes during the early stages of decomposition of readily decom-

possible organic residues in the soil, cannot be doubted. The data in figures 1 and 2 indicating this lag are amply supported in two previous publications (21, 22) and also by the work of Jensen (6), Romell (15), and others. Although different soils do not respond alike to various organic residues, the lapse of time between maximum  $\text{CO}_2$  evolution and maximum microbial development is too great to warrant dependence on the rate of  $\text{CO}_2$  production as an accurate measure of microbial numbers determined by plate counts. The available data and the explanations of other investigators referred to in a previous paper (22) are inadequate to account fully for the cause and significance of this protracted lag period.

The peaks in the  $\text{CO}_2$  curves in figures 1 and 2 show that during the first 10 days of the experiment the Palouse soils were more active than the similarly treated Helmer soils. The total  $\text{CO}_2$  production in comparable samples was

TABLE 1

*Total  $\text{CO}_2$  production and carbon-nitrogen relationships in the various soils and organic residues, based on dry weight*

NUMBER .....	1	2	3	4	5	6	7	8
Substance. . . . .	Helmer untreated	Helmer + Helmer duff	Helmer + Palouse litter	Palouse untreated	Palouse + Palouse litter	Palouse + Helmer duff	Helmer duff	Palouse litter
$\text{CO}_2$ in mgm. of C per kgm. of soil	783.07	1,344.51	1,908.72	788.46	1,953.39	1,332.13		
Total C, per cent ..	2.317	3.345	3.319	3.460	4.304	4.177	36.69	32.64
Total N, per cent	0.100	0.161	0.170	0.209	0.277	0.271	0.578	0.703
C:N ratio	23.17	20.78	19.53	16.54	15.53	15.41	63.45	46.39
Water-soluble C, per cent	0.074	0.144	0.156	0.117	0.198	0.156	2.542	1.765
$\text{H}_2\text{SO}_4$ -soluble C, per cent	0.613	0.840	0.900	0.969	1.287	1.257	9.919	16.886
$\text{H}_2\text{SO}_4$ -insoluble C, per cent	1.619	2.168	2.181	2.264	2.517	2.627	22.779	12.262
$\text{H}_2\text{SO}_4$ -insoluble N, per cent	0.057	0.057	0.060	0.092	0.101	0.100	0.304	0.269
Protein N,* per cent	0.105	0.135	0.139	0.210	0.237	0.236	0.569	0.605

\* Sum of  $\text{H}_2\text{SO}_4$ -soluble and  $\text{H}_2\text{SO}_4$ -insoluble nitrogen.

approximately the same, however, as is indicated in table 1, in which data are presented on total  $\text{CO}_2$  production and on the carbon-nitrogen relationships and carbon fractions of the various soils and organic residues. The greater quantities of water-soluble and sulfuric-acid-soluble carbon in the Palouse soil and Palouse litter may explain these higher peaks, since it is well recognized that these fractions of the organic material in the soil are attacked first. The effect of Palouse litter on  $\text{CO}_2$  evolution in soil 3 as compared with that of Helmer duff in soil 6 is clearly evident.

### *Microbial analysis*

The periodical counts of bacteria, actinomyces, fungi, and aerobic cellulose-decomposing bacteria are illustrated graphically in figures 3, 4, 5, and 6.

A consideration of the bacterial counts recorded in figure 3 and of the total

numbers of microbes illustrated in figures 1 and 2 indicates that, in general, both were considerably lower in the Palouse than in the Helmer soils. In regard to the untreated samples this is contrary to the results reported in the preceding paper (23), which shows that under field conditions both the total microbial population and the population of bacteria were greater in the Palouse soil than in the Helmer soil at the three depths sampled at different times of the year. The effect of the constant optimum moisture and temperature conditions obtaining in the laboratory as compared with the fluctuating temperatures and moisture contents of the soils under their natural

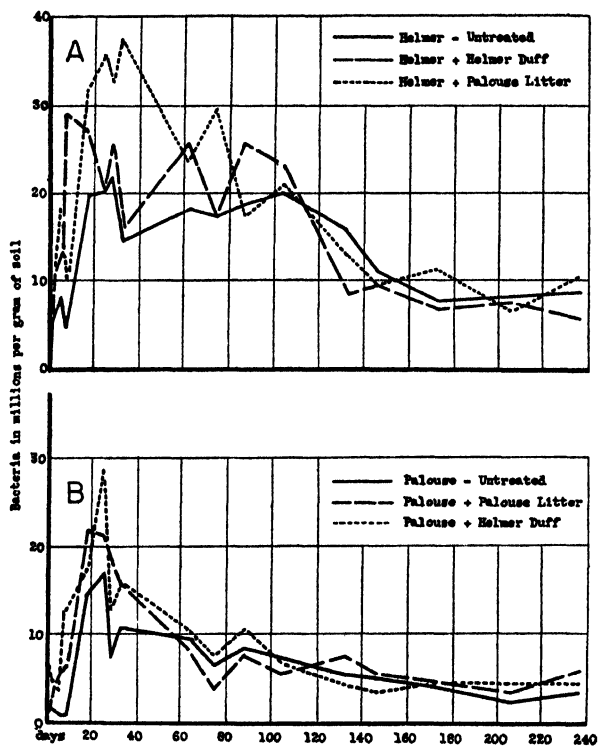


FIG. 3. BACTERIA IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

environment offers a plausible explanation for the observed differences in bacterial behavior. The general rise in bacterial numbers in the untreated samples between the fifth and the twenty-fifth day in the laboratory strengthens this assumption, although a part of this increased activity was due to the decomposition of root material which constitutes a part of the living vegetation under field conditions.

The addition of Helmer duff or Palouse litter to the soils greatly stimulated the development of bacteria during the early stages of organic matter trans-

formation. This effect diminished sharply after the first 15 to 30 days, particularly in the Palouse soils. Some minor peaks in bacterial numbers occurred later in the Helmer soils in which the greater initial stimulating effect of the organic residues was manifested. The Palouse litter in the Helmer soil was considerably more effective in stimulating bacterial growth than was the Helmer duff, but this was not true in the Palouse soil. There the effect of the two residues tended to be in the reverse order, but the difference is small if it is considered that the one exceptionally high count occurring on the twenty-fifth day in soil 6 (Palouse soil treated with Helmer duff) may have

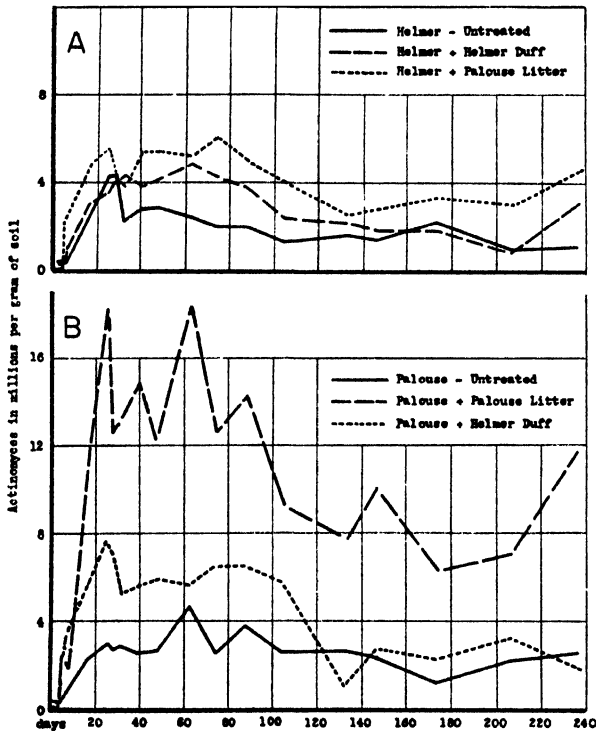


FIG. 4. ACTINOMYCES IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

been partly the result of experimental error. The difference in bacterial activity appeared to be principally the result of differences in the nature of the humus and organic residues in the two soils. The composition of these substances varied considerably, as may be noted from the data in table 1.

The activity of actinomycetes, which is portrayed in figure 4, is interesting. Their growth, like that of the bacteria, was markedly stimulated by the addition of either organic residue to the soil, but the effect of these materials persisted for a longer time. The numbers of actinomycetes were smaller in the untreated Helmer soil than in the untreated Palouse soil, the difference

being in accordance with that observed under field conditions, as reported in the preceding paper (23). Both the inherent character of the soil other than reaction and the nature of the organic residues added were strikingly reflected in their effect on the activity of these organisms. Not only were their numbers much smaller in the Helmer than in the Palouse soil irrespective of treatment, but the difference in effect of the two residues was also very pronounced. The addition of Palouse litter to Palouse soil was exceedingly stimulating, as it caused about a fourfold increase in numbers at the peak of its influence as compared with not much more than a twofold increase resulting from the Helmer duff. The difference was not so marked in the Helmer soil. There the addition of Palouse litter resulted in about a twofold increase in numbers of actinomycetes during the period when its influence was most pronounced, and the effect of Helmer duff in this respect was somewhat less.

The actinomycetes as a group are recognized as being capable of utilizing a wide variety of carbon compounds and protein substances as sources of carbon and energy. It may be noted from the data in table 1 that the sum of the water-soluble and sulfuric-acid-soluble carbon as well as the amount of protein nitrogen is greater for soil 4, the Palouse soil, than for soil 1, the Helmer soil. The larger quantity of these carbon and nitrogen substances may explain the larger numbers of actinomycetes in the Palouse soil. A more careful analysis of the data in table 1 strengthens this point. Both the sum of the water-soluble and the sulfuric-acid-soluble carbon and the amount of protein nitrogen are shown to be greater for the Palouse litter than for the Helmer duff. The Palouse litter proved to be the more effective of the two residues in stimulating actinomycete growth. Soil 5, the Palouse soil with Palouse litter added, had the largest amounts of water-soluble and sulfuric-acid-soluble carbon and protein nitrogen; it also had the greatest actinomycete counts. The same correlation holds for the other treatments, showing the definite influence of the nature of the soil humus and the organic residues added to the soils on the activity of these organisms. The relatively small differences in reaction of the soils which are indicated in figure 9 are unimportant in this respect.

Large numbers of actinomycetes are present in both soils. Their activity, therefore, should play an important part in organic matter transformation, at least in certain cases as will be shown later, although some investigators ignore their presence in the soil and their rôle in decomposition processes. The more recent work of Itano and Arakawa (9), however, emphasizes their importance in biological processes in the soil.

The fungus population, as may be noted from figure 5, was not nearly so large in any of the soils as were the bacterial and actinomycete populations, but it is evident that the Helmer soil is a much better medium for fungus growth than is the Palouse soil. This is shown by the graphs for the untreated soils as well as those for the treated soils and is in agreement with the observations reported previously (23). Both the Palouse litter and the Helmer duff

stimulated markedly the growth of fungi for about the same length of time as they stimulated the growth of actinomycetes. These materials exerted a much more pronounced effect in the Helmer than in the Palouse soil, as during the period of maximum influence they resulted in approximately a threefold increase in numbers of fungi in the Helmer soil and roughly a twofold increase in numbers in the Palouse soil. The stimulating effect of the Helmer duff was greater in both soils than was that of the Palouse litter, indicating that the former is a better food for fungi. Evidently, the nature of the residue on

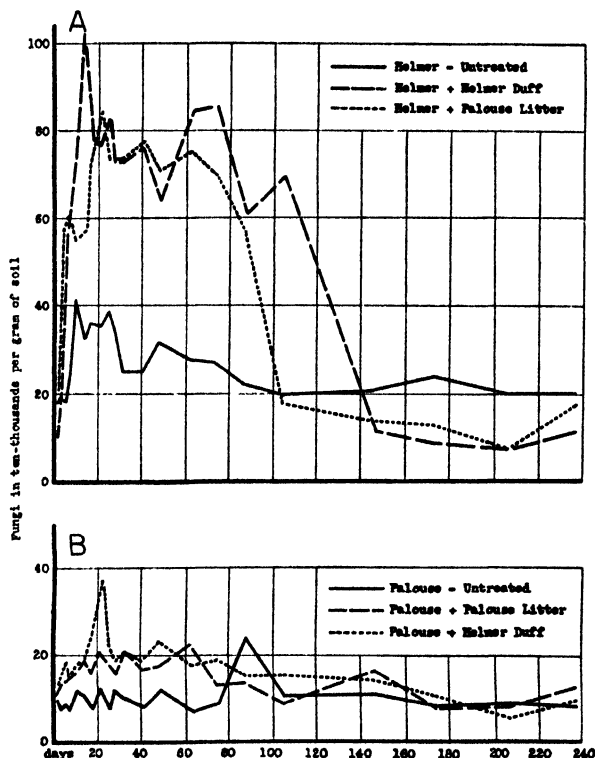


FIG. 5. FUNGI IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

the floors of coniferous forests and the nature of the humus formed from this residue are such as to stimulate fungus growth. Many investigators, including Waksman, et al. (31), Cobb (2), and Powers and Bollen (14), have found that the coniferous floor has large numbers of fungi and that in many cases these forms are the predominating ones in the surface layers.

The cellulose-decomposing bacteria, which were not numerous and which never attained significant numbers in the untreated soils, began to multiply in the treated soils after the maximum peaks had been reached by the other groups of microbes. The data, presented in figure 6, show that the Palouse



soils had the higher numbers and that the variations in effect caused by the two organic residues added to the different soils were not particularly significant. The increases in numbers of cellulose-decomposing bacteria will be discussed later.

The anaerobic nitrogen-fixing bacteria, although present in both soils, never attained large numbers. The importance of their activity here is, therefore, doubtful. On the whole, their development was not stimulated to any sig-

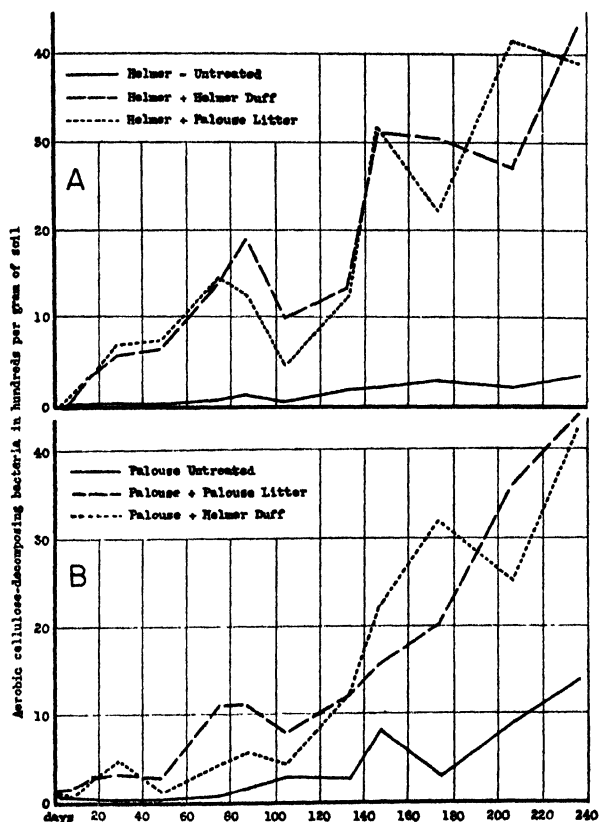


FIG. 6. AEROBIC CELLULOSE-DECOMPOSING BACTERIA IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

nificant degree by the addition of the two organic residues to the soils. Since their numbers, which fluctuated from a few to 200 per gram of dry soil, were about the same as those reported for the same soils in the previous paper (23), they have been omitted here. As stated also in the previous paper, the *Azotobacter* species was not found in these soils.

An examination of figures 3 to 6 discloses not only the influence of the organic food supply and of the soil properties on the type of soil microflora and on the

activity of specific groups of organisms, but also a certain sequence in the activity of the various specific groups of soil microbes. The fungi, except where the numbers were small, attained their peaks in 10 to 15 days. The bacteria reached maximum numbers in 15 to 30 days, depending on the soil. The actinomyces began to reach highest counts only after 25 or more days. The cellulose-decomposing organisms did not greatly increase in numbers until the activity of the other three groups had subsided. It seems evident that both the fungi and the bacteria, particularly the former, were able to compete successfully with the actinomyces for the readily available (probably water-soluble) food supply. The actinomyces, probably suppressed for a short time when readily available food was plentiful, began to rise in numbers when the fungus population and in some cases the bacterial population began to decline. In about 40 days when, as shown in tables 2 and 3, the supply of water-soluble carbon was reduced considerably and the sulfuric-acid-soluble carbon, as well as the water- and acid-soluble nitrogen, was still not materially affected, the aerobic cellulose-decomposing bacteria began to multiply rapidly. The food supply evidently was ample and its nature suitable for their continually increasing multiplication until the termination of the experiment.

Sequential activity of specific groups of microbes in the soil was noted in previous work (21) and has been reported also by Norman (11), Waksman and Starkey (28, pp. 75-101, 244-245), and others. The sequence in activity, the effect of certain groups of organisms on others, and the influence of the nature of the food supply on various specific groups of organisms which were evident in this work are in general agreement with the observations of these investigators.

#### *Organic matter fractionations, pH values, and oxidation-reduction potentials*

The results of the carbon and nitrogen analyses of the various soil extracts intended for fractionation of the organic matter in the six soils at the A, B, C, and D periods mentioned in the experimental procedure are summarized in tables 2 and 3. The relative changes affecting the carbon and nitrogen in the various soil extracts during the course of the experiment are illustrated in figures 7 and 8, in which the amounts of carbon and nitrogen present in the various organic matter fractions at successive time intervals are presented in percentages of the amounts present at the beginning of the experiment.

It is noted in table 2 that in certain soil samples the sum of the percentages of carbon in the various fractions accounts for more than the total, indicating some limitations of the analytical methods used. In most samples, however, the sum of the percentages of carbon in the various fractions ranges between 95 and 99 per cent of the total, showing that the results obtained by the use of the analytical methods as described in the experimental procedure are at least as reliable as those indicated by the available data on sugar determinations in the water- and acid-soluble fractions. The sum of the percentages of nitrogen in the various extracts listed in table 3 also exceeds the total amount

of nitrogen in the soil in some cases, but, on the whole, the results show a satisfactory recovery of nitrogen by this method of fractionation.

Various investigators including Starkey (17), Waksman and Tenney (30), Tenney and Waksman (20), and Hutchings and Martin (5) hold that the rate of decomposition of organic residues depends upon their chemical composition. For example, residues rich in nitrogen and relatively poor in cellulose,

TABLE 2  
*Organic carbon fractions, in per cent of oven-dried soil*

SOIL NUMBER*	TOTAL C	WATER-SOLUBLE C	H <sub>2</sub> SO <sub>4</sub> -SOLUBLE C	H <sub>2</sub> SO <sub>4</sub> -INSOLUBLE C	SUM OF C FRACTIONS	PER CENT OF TOTAL C ACCOUNTED FOR
A 1	2.317	0.074	0.613	1.619	2.306	99.52
2	3.345	0.144	0.840	2.168	3.152	94.24
3	3.319	0.156	0.900	2.181	3.237	97.53
4	3.460	0.117	0.969	2.264	3.350	96.83
5	4.304	0.198	1.287	2.517	4.002	92.69
6	4.177	0.156	1.257	2.627	4.040	96.71
B 1	2.145	0.080	0.645	1.582	2.307	107.58
2	3.253	0.111	0.796	2.331	3.238	99.48
3	3.204	0.117	0.850	2.032	2.999	93.61
4	3.529	0.087	1.128	2.253	3.468	98.29
5	3.937	0.129	1.278	2.464	3.871	98.31
6	4.025	0.138	1.226	2.636	4.000	99.41
C 1	2.080	0.064	0.559	1.479	2.102	101.08
2	3.225	0.083	0.862	2.092	3.037	94.14
3	3.075	0.112	0.897	2.046	3.054	99.36
4	3.478	0.089	1.047	2.248	3.383	97.30
5	3.844	0.108	1.217	2.460	3.785	98.47
6	4.027	0.129	1.268	2.538	3.935	97.69
D 1	2.204	0.054	0.462	1.481	1.997	90.65
2	2.992	0.076	0.756	2.151	2.983	99.69
3	2.847	0.086	0.799	2.117	3.002	105.42
4	3.300	0.095	0.956	2.190	3.241	98.23
5	3.838	0.109	1.061	2.419	3.589	93.35
6	3.906	0.108	1.085	2.480	3.673	94.01

\* Letters A to D indicate progressive periods of sampling: A, beginning; B, 40 days; C, 104 days; D, 236 days.

such as legume hays, decompose faster than materials relatively poor in nitrogen and rich in cellulose. Waksman and Starkey (28, pp. 75-101, 244-245) and Watson (32), among others, give evidence of the well-recognized fact that in the process of decomposition of organic materials the water-soluble fraction is attacked first, followed in order by the proteins, hemicelluloses, and celluloses. Decomposition then becomes less rapid, because of the relative increase

of the less easily decomposable substances, such as fats, waxes, resins, lignins, and synthesized microbial products which include some of these substances. The greater the amounts of the more readily available fractions in plant materials, as in young plants, for instance, the more rapid their decomposition should be. The composition and age of plant materials, however, are not the only factors influencing their decomposition. The types and numbers of

TABLE 3  
*Nitrogen fractions, in per cent of oven-dried soil*

SOIL NUMBER*	TOTAL N	WATER- SOLUBLE† N	H <sub>2</sub> SO <sub>4</sub> - SOLUBLE N	H <sub>2</sub> SO <sub>4</sub> - INSOLUBLE N	NITRATE N	SUM OF N FRACTIONS	PER CENT OF TOTAL N ACCOUNTED FOR	PROTEIN‡ N
A 1	0.100	0.002	0.048	0.057	0.000	0.107	106.71	0.105
2	0.161	0.013	0.078	0.057	0.015	0.163	101.86	0.135
3	0.170	0.014	0.079	0.060	0.016	0.169	99.41	0.139
4	0.209	0.006	0.118	0.092	0.000	0.216	103.44	0.210
5	0.277	0.020	0.136	0.101	0.018	0.275	99.20	0.237
6	0.271	0.021	0.136	0.100	0.016	0.273	100.62	0.236
B 1	0.093	0.003	0.034	0.058	0.002	0.097	103.97	0.092
2	0.166	0.012	0.070	0.071	0.017	0.170	98.09	0.141
3	0.173	0.013	0.077	0.071	0.017	0.178	107.95	0.148
4	0.214	0.006	0.112	0.095	0.005	0.218	101.94	0.207
5	0.273	0.016	0.132	0.106	0.015	0.269	98.93	0.238
6	0.270	0.017	0.132	0.105	0.018	0.272	102.99	0.237
C 1	0.100	0.003	0.043	0.055	0.004	0.105	105.01	0.098
2	0.166	0.010	0.064	0.067	0.020	0.161	97.35	0.132
3	0.170	0.007	0.071	0.071	0.023	0.172	101.17	0.142
4	0.217	0.005	0.108	0.093	0.009	0.215	99.21	0.201
5	0.266	0.007	0.118	0.103	0.003	0.231	97.70	0.221
6	0.267	0.008	0.114	0.105	0.003	0.230	96.96	0.219
D 1	0.092	0.001	0.031	0.052	0.006	0.090	98.53	0.083
2	0.146	0.003	0.046	0.066	0.023	0.138	94.74	0.112
3	0.154	0.004	0.062	0.067	0.022	0.155	100.85	0.129
4	0.205	0.005	0.090	0.091	0.010	0.196	95.49	0.181
5	0.261	0.007	0.100	0.097	0.040	0.244	93.83	0.198
6	0.252	0.007	0.097	0.101	0.040	0.245	97.33	0.198

\* Letters A to D indicate progressive periods of sampling: A, beginning; B, 40 days; C, 104 days; D, 236 days.

† Exclusive of nitrate nitrogen.

‡ Sum of the H<sub>2</sub>SO<sub>4</sub>-soluble and H<sub>2</sub>SO<sub>4</sub>-insoluble nitrogen.

microbes present also play a leading rôle in this process. It is generally accepted, for example, that fungi attack cellulose readily in the presence of available nitrogen, that bacteria decompose sugars readily even in the presence of small amounts of available nitrogen, and that actinomyces can utilize the

carbon of both carbonaceous and nitrogenous substances. Obviously, the mineralization of organic residues is a complex process depending on a variety

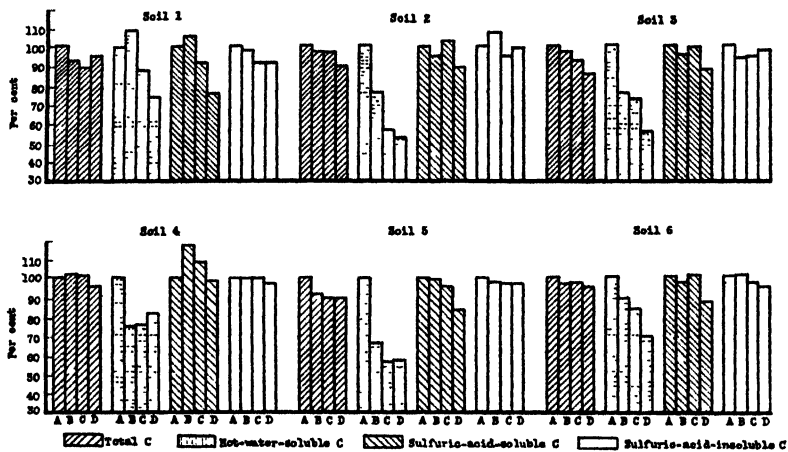


FIG. 7. ORGANIC CARBON FRACTIONS IN PERCENTAGES OF THE AMOUNTS PRESENT IN THE SOIL AT THE BEGINNING OF THE EXPERIMENT

A, at the beginning; B, at 40 days; C, at 104 days; and D, at 236 days

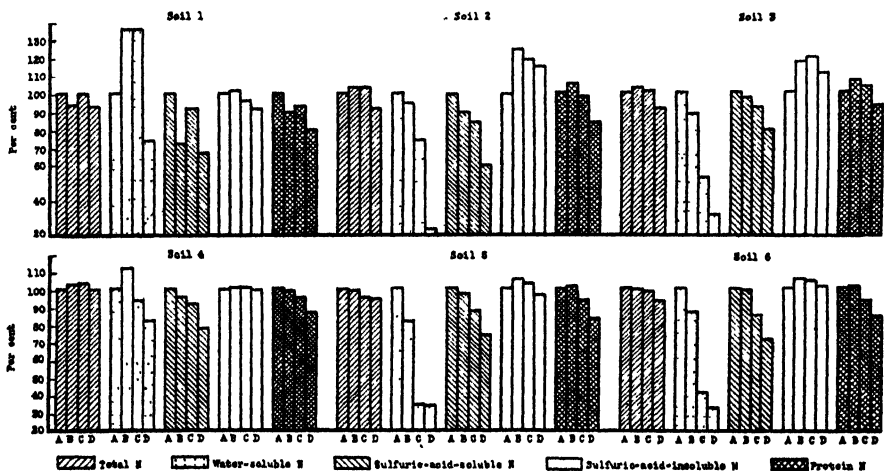


FIG. 8. NITROGEN FRACTIONS IN PERCENTAGES OF THE AMOUNTS PRESENT IN THE SOIL AT THE BEGINNING OF THE EXPERIMENT

A, at the beginning; B, at 40 days; C, at 104 days; and D, at 236 days

of closely related factors. Although most of the available evidence regarding the nature of organic matter decomposition is based on the results of experiments with small quantities of various organic residues, pure or heterogeneous,

used alone or mixed with sand, and inoculated with pure or mixed cultures of soil microbes, or soil suspensions, the soil serving merely as an inoculant and not as a medium for microbial activity, the results of this investigation, in which the soil was used as the medium for microbial activity, bear out at least some of the foregoing observations, as will be pointed out.

A comparison of the amounts of carbon and nitrogen in the untreated soils, soils 1 and 4, reveals that the Palouse soils contained more protein nitrogen, and more water-soluble and sulfuric-acid-soluble carbon and nitrogen than did the Helmer soils. The data in table 1 show that the Palouse litter also contained larger amounts of these carbon and nitrogen substances than did the Helmer duff, although probably a part of the readily available materials, such as water-soluble and possibly sulfuric-acid-soluble substances, had been decomposed already, since these residues were collected from the surface of the soils. The relationship of some of these compounds to the activity of the bacteria, fungi, and actinomyces in particular has already been pointed out.

The total carbon content as shown in table 2 and figure 7 decreased in all soils. This was to be expected, since  $\text{CO}_2$ , the most important measurable by-product in organic matter transformation in the soil, was liberated. An exact comparison of the loss of carbon with the amounts of  $\text{CO}_2$  produced and the total numbers of microbes in the soil is not possible, because of the limitations of the analytical methods and also because different specific groups of microbes do not use equal quantities of the carbon liberated from the organic materials broken down by them. It is well known, for example, that the fungi as a group utilize liberated carbon more efficiently than do the bacteria as a group. Nevertheless, general relationships are evident. The soils which lost the largest amounts of carbon, as soils 2, 3, 5, and 6, also produced the largest total amounts of  $\text{CO}_2$  and had the largest microbial populations, although as has been pointed out before, there was a considerable lag between maximum evolution of  $\text{CO}_2$  and maximum numbers of organisms.

The data in table 2 and figure 7 also indicate that the water-soluble carbon in soils 2, 3, 5, and 6, which received the organic residues and contained the largest amounts of this carbon, decreased more rapidly and to a greater extent than did the other fractions. This is in accordance with the observations of the aforementioned investigators and of other workers in the field of organic matter transformation. The greatest loss of water-soluble carbon in all the soils, except soil 1, occurred in the earlier stages of decomposition during the A period when microbial activity, particularly that of the bacteria and fungi, was at a maximum. The discrepancy in soil 1 and, to a certain extent, that in soil 2 may be due to experimental error.

The sulfuric-acid-soluble carbon, which comprised 25 to 30 per cent of the total carbon, evidently was much more resistant to decomposition in the soil than was the water-soluble carbon. The sulfuric acid extract contains among other carbon compounds hemicellulose and cellulose. Since hemicelluloses are synthesized by soil microbes, it is likely that although the cellulose in

the sulfuric-acid-extracted fraction was decomposed rapidly, the newly synthesized hemicellulose accumulating as a by-product of microbial activity obscured the actual changes which took place in the carbon of this fraction. Although the percentage breakdown of carbon in this fraction was relatively small in comparison with that in the water-soluble fraction, the total amounts lost, as shown in table 2, are considerable, indicating that the sum total of the decomposing and synthesizing activities favored the former. Again the results obtained from soils 1 and 4 appear to be erratic, as they were with respect to the water-soluble carbon. If these discrepancies are disregarded, it is noted that the greatest loss occurred in soils 5 and 6 which, according to the data in figures 3 and 4, also had the largest numbers of actinomyces, as well as large numbers of bacteria. This suggests that the sulfuric-acid-soluble carbon fraction, which also contains considerable quantities of nitrogenous substances, as indicated in table 3, is, as has been pointed out, a more suitable food for actinomyces than for bacteria and fungi. The loss of sulfuric-acid-soluble carbon in these soils as well as in the other two receiving organic residues continued after 104 days, the C period. At that time the activity of the actinomyces declined rapidly and the numbers of aerobic cellulose-decomposing bacteria began to increase rapidly and continued their ascendancy until the end of the experiment, evidently indicating that a plentiful supply of cellulose was still available at that time.

The sulfuric-acid-insoluble carbon fraction, which comprised from 63 to 74 per cent of the total carbon, contained some cellulose, lignins, and other difficultly decomposable compounds. The carbon in this fraction proved to be the most resistant to decomposition, a fact which is generally accepted. Although the percentage reduction of carbon in this fraction was small, regardless of treatment, and, therefore, was insignificant from this standpoint, the total amounts lost, as may be noted from the data in table 2, were as large as and in certain cases larger than those lost from the water-soluble fraction, indicating that some decomposition was taking place.

The data on the changes in nitrogen content of the various soil extracts obtained at the four successive sampling periods are presented in table 3 and figure 8. A small reduction in the supply of total nitrogen occurred during the course of the experiment. Since no *Azotobacter* and only a few anaerobic nitrogen-fixing bacteria were present in these soils, no increase in total soil nitrogen was expected. To be sure, the absolute accuracy of the Kjeldahl method may be questioned, but the observed loss of nitrogen, though small and difficult to account for, appeared to be too consistent to be accidental. Similar results obtained under similar conditions were reported in a previous publication (22) in which it was pointed out that the reduction in total nitrogen was not caused by the loss of ammonia, since no appreciable quantities of this substance were found to escape from the soil. The cause of the small loss of nitrogen observed in these experiments is still obscure.

The water-soluble nitrogen, as may be noted from figure 8, decreased rapidly

and to a marked extent in every soil, and particularly in the soils treated with organic residues. In some of the latter soils only a small percentage remained at the end of the experiment. The nitrogen in this fraction consisted of ammonia, amino acid, and water-soluble protein. It did not include nitrate nitrogen, as this was determined and accounted for separately. The ammonia nitrogen, although included in the water-soluble fraction, was also determined separately. The results of the determinations of both of these compounds are recorded in table 4.

The data in table 4 show that although the amounts of ammonia and nitrate nitrogen decreased rapidly during the early stages of decomposition of the organic residues in soils 2, 3, 5, and 6, an abundant supply was available at all times, even when microbial numbers were at a maximum. Moreover, it is evident that as the ammonia nitrogen decreased in quantity after the first 17 days the amounts of nitrate nitrogen increased rapidly, showing that nitrification in these soils was very active. Larger amounts of nitrate nitrogen

TABLE 4  
*Nitrate and ammonia nitrogen, in parts per million of oven-dried soil*

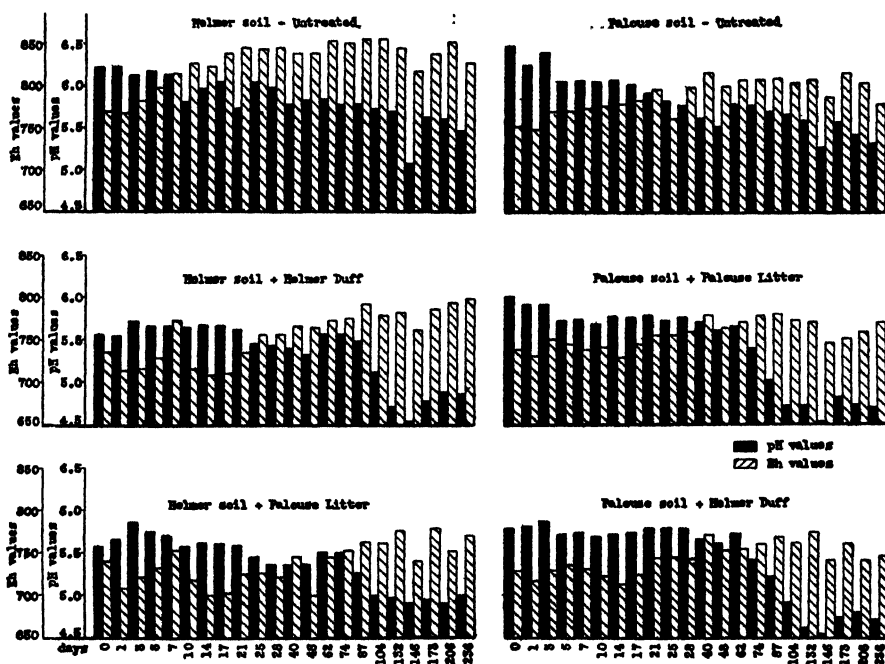
DAYS	1		2		3		4		5		6	
	Helmer untreated		Helmer + Helmer duff		Helmer + Palouse litter		Palouse untreated		Palouse + Palouse litter		Palouse + Helmer duff	
	NO <sub>3</sub> -N	NH <sub>3</sub> -N	NO <sub>3</sub> -N	NH <sub>3</sub> -N	NO <sub>3</sub> -N	NH <sub>3</sub> -N	NO <sub>3</sub> -N	NH <sub>3</sub> -N	NO <sub>3</sub> -N	NH <sub>3</sub> -N	NO <sub>3</sub> -N	NH <sub>3</sub> -N
0	1.2	16.6	153.8	80.0	156.8	140.6	2.58	42.9	177.7	138.1	160.0	153.9
7	3.6	14.2	150.9	50.0	145.4	72.8	6.60	48.0	150.9	138.1	140.3	154.0
17	12.5	20.7	133.3	57.2	145.4	50.7	25.00	30.0	140.3	125.1	140.3	133.5
40	23.8	12.0	166.6	38.1	166.6	48.5	48.10	11.5	154.3	102.7	179.5	111.1
104	44.4	11.8	205.1	53.3	228.5	40.0	86.00	10.3	320.0	14.5	320.0	80.0
236	61.5	8.0	235.2	10.7	216.2	11.5	102.50	6.16	400.0	10.0	400.0	10.0

accumulated in the Palouse soils than in the comparable Helmer soils. This was to be expected, since in the former the C:N ratios were narrower, as indicated in table 1, and the amounts of water- and acid-soluble-nitrogen were larger than in the latter. It is noted also that during the first 40 days when the fungus population was largest, the ammonia in soils 2 and 3, the Helmer soils, disappeared more rapidly than in soils 5 and 6, the Palouse soils. Since the fungus population in the two Helmer soils was about three times as large as that in the two Palouse soils, it is likely that these organisms were responsible for the greater loss of ammonia from the Helmer soils. As indicated in figure 8, the nitrogen content of the sulfuric-acid-insoluble fraction in these two soils built up with time, whereas it did not change appreciably in the two Palouse soils. According to previous results (21) as well as to those of Waksman (24), Sturgis (19) and others, it appears that in the process of decomposition of organic residues in the soil the nitrogen content of the sulfuric-acid-insoluble fraction of the organic matter tends to increase as a result of



synthesis of microbial protoplasm. Both the Helmer and the Palouse soils supported a large bacterial flora, but apparently more microbial protoplasm was produced in the treated Helmer soils with their comparatively large fungus population and small numbers of actinomyces than in the similarly treated Palouse soils with their comparatively small fungus population and large numbers of actinomyces.

The sulfuric-acid-soluble nitrogen, as may be noted from the data in figure 8, decreased in about the same ratio in all the soils, indicating that the protein substances in this fraction of the organic matter in the various soils were



influence in bringing about the observed differences in microbial activity. A consistent increase in acidity with time took place in all the soils. A similar increase in acidity noted in previous work (22) of a similar nature was attributed to the accumulation of nitrate nitrogen. Watson (32) also observed an increasing acidity of the soil as a result of organic matter decomposition processes. More recently Stephenson (18) found that changes in soil reaction under field conditions follow closely upon changes in nitrate nitrogen accumulation. The production of various organic acids in the process of organic matter decomposition is well recognized, but it is questionable whether these accumulate sufficiently in the soil under aerobic conditions to affect the reaction appreciably. A more plausible explanation for the increased acidity observed in the soils in this experiment is the accumulation of nitrate nitrogen.

The results of the oxidation-reduction potential determinations are also shown in figure 9, in which it is indicated that the Eh values were lower for the treated soils than for the corresponding untreated soils. The studies reported in the preceding paper (23) on the Eh values at different depths of the same Palouse and Helmer soils under field conditions pointed to definitely and consistently lower values in the upper soil layers, particularly the surface organic layer. Reserves of reducing substances in the organic layer of these soils were presumed to be the cause of the observed lower Eh values. The addition of the surface organic residues of these same soils to the soil samples in this experiment would be expected to produce a drop in the Eh values of these samples, because of the reserves in reducing substances thus incorporated. Evidently such was the case. Another consistent trend indicated in figure 9 is that the Eh values of all the soils, although fluctuating somewhat as did the pH values, increased gradually with time. Heintze (3), and Peech and Batjer (12) noted that high oxidation-reduction potentials of soils are associated with low pH values. The general decrease in the pH values and the coincident increase in Eh values (fig. 9) are in agreement with their observations with respect to the reciprocity of pH and Eh values, but the rising Eh values correspond also with a diminishing supply of organic matter as decomposition proceeded, suggesting a decrease in reserves of reducing substances. It is noticed also that in general the gradual increase in Eh values is more pronounced for the Helmer soils than for the Palouse soils, and for the Helmer-duff-treated Helmer and Palouse soils than for the Palouse-litter-treated Helmer and Palouse soils. These tendencies suggest that the reserve supply of reducing complexes was greater or more active in the Helmer duff and humus. There was no correlation between the observed variations in Eh values and the striking differences in microbial activity in the variously treated soils.

#### DISCUSSION

The profile characteristics of the Helmer and Palouse soils, vary considerably, though these soils have developed from identical parent material under the same climatic conditions.

Helmer silt loam, a brown colored forest soil, has at the surface a layer of duff ranging from 0.5 to 1.5 inches in thickness. It is underlain by an  $A_1$  horizon, 0.5 to 1.5 inches in thickness and consisting of gray, rather fluffy mineral material mixed with organic matter. The description of Helmer silt loam by Agee, et al. (1) and that of the closely related Santa silt loam by Poulson and Platt (13) do not refer to this layer, which, nevertheless, is present though not everywhere continuous. The underlying  $A_2$  horizon, 6 to 8 inches in thickness, is grayish yellow-brown, somewhat compact, and is underlain by a browner though still grayish mottled and very compact  $B_1$  horizon which extends to a depth of 22 inches. The  $B_2$  horizon, extending from the depth of 22 to between 50 and 60 inches, is slightly less compact, somewhat mottled by clay and sesquioxide illuviation, and is of a tawny yellow-brown color approaching that of the underlying parent material. There is no evidence of calcium carbonate accumulation or of prismatic or columnar structure. In general, the profile characteristics of Helmer silt loam indicate that this soil is closely related to the brown forest soils described by Joffe (7, p. 315-325).

Palouse silt loam, a grassland soil, has relatively little organic residue on its surface. The  $A_1$  horizon, extending to a depth of 4 inches, is brown-black, somewhat laminar, friable, and granular. The  $A_2$  horizon, which is generally about 12 inches thick and is thicker on certain slopes, has a grayish dark brown color and a granular, crumbly structure. It is underlain by an 8- to 10-inch layer of light brown compact material of crumbly structure, called the  $A_3$  horizon by Poulson and Platt (13). The B horizon extending from the depth of 24 inches to 40 or 50 inches is yellowish-brown compact material showing little tendency to form columns or prisms, although in certain profiles a prismatic structure is evident. The underlying material is free from calcium carbonate, which may be present, however, in certain profiles, depending upon slope and exposure of the land. The profile characteristics of Palouse silt loam used in this investigation indicate that this soil is closely related to the prairie soils.

There is no indication of a former grass type of vegetation on the Helmer soil. If at some time in the past the prairie encroached on the forest, the time is so remote that all traces of an original grassland vegetation have disappeared. The reverse holds true for the Palouse soil.

Vegetation has played a fundamental rôle in differentiating the characteristics of these two soil types, especially those characteristics concerning the amount of humus, the microflora, the soil color, and the soil structure. A consideration of the vegetation is not complete, however, unless both the top growth and the root development receive attention. It is reasonable to suppose that on identical soil materials under the same climatic conditions, at least as much vegetative material, including top and root growth, is produced annually by forest vegetation as by grass vegetation, because the loss of moisture by evaporation is smaller under forest cover than under grass cover. Tree roots withdraw moisture from greater depths in the soil than do grass

roots, and in areas where rainfall is scarce during the summer months, tree vegetation has a longer annual growth period than has grass vegetation. Determinations were made of the annual top growth vegetation on the Palouse soil and of the root material in the surface 10 inches of both the Palouse and the Helmer soils. The results are given in detail in the preceding paper (23), but some of the more pertinent data together with estimates (26, p. 221-226) for the top growth on the Helmer soil are reproduced in table 5, from which the following deductions and comparisons may be made.

The amount of top growth on the Helmer soil (based on estimates) is nearly twice that on the Palouse soil. The amount of root material in the surface 4 inches of the Palouse soil is more than double that in the same layer of the Helmer soil. The difference between the amounts of root material in the 4- to 10-inch layers of the two soils is relatively small. Contrary to the fore-

TABLE 5

*Amounts and composition, based on dry weight, of annual top growth and root materials for Palouse and Helmer silt loam*

SUBSTANCE	HELMER SOIL	HELMER DUFF	HELMER SOIL ROOTS			PALOUSE SOIL	PALOUSE LITTER	PALOUSE SOIL ROOTS		
			Depth, in inches					Depth, in inches		
			0-4	4-10	0-10			0-4	4-10	0-10
Top growth, tons per acre	1.37*					0.71				
Roots, tons per acre			2.29	2.38	4.67			5.16	1.95	7.11
Total C, per cent		36.69			48.11		32.64			42.15
Total N, per cent		0.578			0.425		0.703			0.585
C N ratio		63.45			113.20		46.39			72.05
H <sub>2</sub> O- and H <sub>2</sub> SO <sub>4</sub> -soluble C, per cent		12.46			13.51		18.65			14.65
H <sub>2</sub> SO <sub>4</sub> -insoluble C, per cent		22.78			26.92		12.26			21.47
H <sub>2</sub> O- and H <sub>2</sub> SO <sub>4</sub> -soluble N, per cent		0.309			0.195		0.383			0.351
H <sub>2</sub> SO <sub>4</sub> -insoluble N, per cent		0.304			0.193		0.269			0.194

\* Based on average figures from Waksman (26, p. 221-226).

going assumption, that as much vegetative material should be produced on forest as on grassland soils, there is a somewhat greater quantity of top and root material on the Palouse soil than on the Helmer soil. Although not known with certainty, the fine root material in the grassland soils may decompose more rapidly than the relatively coarse roots in the forest soils, and the generation time of the root system may be shorter for grass vegetation than for tree vegetation. These comparisons, though based on tentative data and estimates requiring verification by more extensive investigations, are highly indicative of significant differences in the amounts and types of vegetative materials annually returned to the Palouse and the Helmer soils.

The root material together with the top growth constitutes the major supply of potential organic substance which is eventually transformed to humus under virgin soil conditions. The apparently greater amount of top and root material returned annually to the Palouse soil as compared with that returned

to the Helmer soil and the seemingly more rapid turnover of the grass root system of the former are factors contributing to the difference in humus content in favor of the Palouse soil, but they are not the only factors involved and perhaps not the most influential ones. The composition of the organic residue undoubtedly is another important factor in the transformation of this residue to humus.

It is noted from the data in tables 1 and 5 that the Palouse litter and roots contain more water-soluble and sulfuric-acid-soluble carbon and nitrogen, and less sulfuric-acid-insoluble carbon and nitrogen than do the Helmer duff and roots. The carbon-nitrogen ratios of the Palouse litter and roots respectively are much narrower than those of the Helmer duff and roots. Since the water-soluble and sulfuric-acid-soluble compounds of organic residues decompose much more readily than do the sulfuric-acid-insoluble compounds, as has been pointed out, it might be expected that the top and root materials of the Helmer soil would decompose more slowly than those of the Palouse soil. That such is the case even in the presence of an ample supply of nitrogen was demonstrated in this investigation insofar as decomposition processes can be measured by changes in the carbon compounds. Moreover, the data on  $\text{CO}_2$  evolution and total organic carbon in tables 1 and 2 show a greater loss of carbon from soils 4 and 5, the untreated and Palouse-litter-treated Palouse soil respectively, than that from soils 1 and 2, the comparably treated Helmer soils. Yet, the humus content of the Helmer soil proved to be only about two thirds as large as that of the Palouse soil, a difference too large to be fully accounted for by the presumed relatively small difference between the amounts of vegetative residues received annually by these soils. How, then, can this apparent anomaly be explained?

It is significant that the differences in carbon and nitrogen contents of the various extracts obtained from the plant materials of the Palouse and the Helmer soils are not reflected in the same manner in comparable extracts from the humus of these soils. The organic residues (tops and roots) and humus of the Palouse soil contain more water-soluble and sulfuric-acid-soluble carbon and nitrogen than do the same substances of the Helmer soil, but the sulfuric-acid-insoluble carbon and nitrogen, constituting by far the largest percentages of the total carbon and nitrogen and present in much larger percentages in the Helmer duff and roots than in the Palouse litter and roots, occur in similar percentages in the humus of the corresponding soils. The difference between the nature of the humus of the two soils and their corresponding organic residues must be attributed to differences in the process of organic matter transformation, initiated and carried on chiefly by the soil microflora, which is composed predominantly of bacteria and actinomycetes in the Palouse soil and of bacteria and fungi in the Helmer soil. Evidently the nature of the humus, disregarding the amount produced from different organic residues, is a function of the particular type of microflora responsible for the decomposition of these residues.

In a consideration of the amount of humus that can be formed per unit of organic material, the carbon-nitrogen ratio of the organic material probably is more important than the type of microflora decomposing the material. Evidence presented in a previous paper (4) leads to the conclusion that under like climatic conditions the aerobic process of transformation of organic residues varying widely in carbon-nitrogen ratios tends to result in the formation of humus with a definite, uniform carbon-nitrogen ratio, indicating that the quantity of humus produced from organic residues is inversely proportional to the carbon-nitrogen ratio of the residues. The carbon-nitrogen ratios of the Helmer duff and roots are much wider than those of the Palouse litter and roots; hence, less humus is formed per unit of vegetative material in the Helmer soil than in the Palouse, provided the carbon-nitrogen ratio in the humus of these soils varies but slightly, as is probable since both soils are formed under the same climatic conditions. The carbon-nitrogen ratios recorded in table 1 are not the ratios for humus, because the carbon values include carbon of live roots and other organic substances in the initial stages of decomposition. The latter, as has been mentioned, are present in greater amounts in the Helmer soil than in the Palouse. Thus, it appears that one of the chief causes of the relatively small percentage of humus in the Helmer soil is the relatively small amount of humus formed per unit of vegetative material. Another probable contributory factor is, as pointed out by Joffe (7, pp. 225-235, 259-261), that grass vegetation contains a larger percentage of ash and bases than does coniferous forest vegetation. The decomposing grass vegetation liberates enough bases to flocculate the organic decomposition products, thereby greatly decreasing their loss by leaching, whereas the decomposing coniferous vegetation liberates an insufficient amount of bases to coagulate the by-products of decomposition, which consequently remain in suspension and suffer loss by leaching to lower horizons.

The aforementioned differences in composition and decomposition of the organic residues result in a relatively efficient humus formation, a comparatively large actinomyces population, a dark color, and a granulated structure in the Palouse soil, in contrast with a less efficient humus formation, a more acid reaction, a comparatively large fungus population, a lighter color, and comparatively little granulation in the Helmer soil. The rôle of the microflora in these processes is very markedly influenced, one might say controlled, by the nature of the organic residues. This was demonstrated by the fact that in the Helmer soil the activity of bacteria and actinomyces was stimulated more and that of the fungi less by Palouse litter and by Helmer duff, and that the effects were in the reverse order in the Palouse soil. If soil material is subjected to different vegetative covers under similar climatic conditions, it may be expected that under forest vegetation, such as covers the Helmer soil, the decomposition of forest organic matter, which is low in bases, will tend to lower the pH value of the medium, and because of the nature of the decomposing organic matter the fungus population, favored from the beginning,

will become further stimulated as the soil develops. Under grass vegetation, such as covers the Palouse soil, the decomposition of the grass organic matter, which is higher in bases, will tend to maintain the pH value of the soil material near the neutral point, and because of the nature of the decomposing organic matter the actinomyces population, large from the beginning, will be increased further as the soil develops. Where the reaction of the two types of soil formed is only slightly acid and varies but little, as in the Palouse and the Helmer soils, the bacteria, though numerous in the soil material from the beginning, will be stimulated more by the organic residues of higher base content than by those of lower base content. The particular type and activity of the soil microflora thus established, chiefly through the nature of the plant residues that are supplied, play an important rôle in the development of specific inherent soil properties during the course of soil formation. Thus, the kind of vegetation and, hence, the quantity and nature of the organic residues added to identical soil materials exposed to similar climatic conditions will result in the production of different amounts of humus and in the development of diverse types of microflora, which, in turn, will produce dissimilar organic decomposition products and types of humus. The influence of these factors is paramount in the differentiation of such inherent soil characteristics as humus content, reaction, color, and structure.

#### SUMMARY

Virgin Helmer and Palouse silt loams taken from the surface 10 inches were used for microbial and chemical studies of untreated samples of soil, of samples treated with their homologous organic residue, and of samples of one soil treated with the organic residues of the other soil.

The maximum daily  $\text{CO}_2$  evolution occurred during the first day and was greater in Palouse soil and Palouse litter than in Helmer soil and Helmer duff, corresponding with the relatively larger amounts of water-soluble and sulfuric-acid-soluble carbon in the humus and surface organic residue of the former soil. There was a lag of 2 or 3 weeks between maximum  $\text{CO}_2$  production and maximum numbers of microbes, indicating that  $\text{CO}_2$  production was by no means an accurate index of microbial numbers.

The Helmer soils supported larger numbers of fungi and bacteria, and smaller numbers of actinomyces than did the corresponding Palouse soils. In the Helmer soils the fungi were stimulated more, and the bacteria and especially the actinomyces less, by the addition of Helmer duff than by the addition of Palouse litter. In the Palouse soils the actinomyces were stimulated much more, and the bacteria and fungi less by the addition of Palouse litter than by the addition of Helmer duff.

The aerobic cellulose-decomposing bacteria although few in number were stimulated markedly in both soils by the addition of organic residues. No *Azotobacter* and only small numbers of anaerobic nitrogen-fixing bacteria were found in these soils, irrespective of treatment.

In the process of decomposition of the organic residues the fungi reached maximum numbers first, followed closely by the bacteria, later by the actinomyces, and finally by the aerobic cellulose-decomposing bacteria. The bacteria and fungi appeared to be chiefly responsible for the decomposition processes in the Helmer soils, and the bacteria and actinomyces for these processes in the Palouse soils.

The water-soluble carbon and nitrogen decomposed very rapidly, particularly during the time when the bacteria and fungi were most active. The sulfuric-acid-soluble carbon and nitrogen proved to be more resistant to decomposition, but the loss was greatest in the soils with the largest numbers of actinomyces, suggesting that these substances constitute a more suitable food for actinomyces than for bacteria and fungi. The decrease in sulfuric-acid-insoluble carbon was very small, and a slight gain in sulfuric-acid-insoluble nitrogen was realized in certain soils, probably because of protein synthesis by the microflora.

The roots and surface organic residue of the Palouse soil contained more water-soluble and sulfuric-acid-soluble carbon and nitrogen and less sulfuric-acid-insoluble carbon and nitrogen than did the corresponding substances of the Helmer soil, whereas the humus in the Palouse soil, as compared with that in the Helmer soil, contained not only more water-soluble and sulfuric-acid-soluble carbon and nitrogen but also similar percentages of sulfuric-acid-insoluble carbon and nitrogen. The latter were attributed to differences in type and activity of the microflora.

A small but consistent loss of nitrogen from all the soils was observed. Larger amounts of nitrate nitrogen accumulated in the Palouse soils than in the similarly treated Helmer soils. The ammonia nitrogen content of the soils decreased rapidly as their nitrate nitrogen content increased, and this was associated with a gradual reduction in pH values. The oxidation-reduction potentials were lower in the treated soils than in the untreated soils and increased in all soils with the decrease in pH values and organic matter.

The influence of vegetation on the type and activity of the microflora that is likely to prevail, and the nature of humus and inherent soil characteristics that may result in soils developed from identical parent materials under similar climatic conditions are discussed.

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## BOOK REVIEWS

*Principles of Feeding Farm Animals.* Revised Edition. By SLEETER BULL AND W. E. CARROLL. The Macmillian Company, New York, 1937. Pp. xi + 395, figs. 60, tables 22. Price \$2.90.

Studies carried out by the Federal Department of Agriculture in 1922-23 showed that approximately three quarters of the product of crop land is used for the feeding of farm animals. This is aside from our humid pastures and the arid and semiarid grazing lands. It has been pointed out by a number of investigators that the mechanization of our farms has led to the elimination of horses and mules equivalent to the produce of 25 to 40 millions of acres. At the same time, it is widely recognized that the efficiency of our meat and dairy animals has been very substantially increased in respect to the utilization of animal foods. Altogether, we are dealing with an economic factor of wide significance.

The present volume is a timely contribution to the subject. It will be of more direct value to the students in our vocational schools and our colleges, and, likewise, to livestock producers, than to the more advanced students of animal nutrition. This fact is noted by the authors in the preface to their book, as follows: "An effort has been made to present the scientific facts underlying the art of feeding animals in such a manner that the book will not only be suitable for use as a text for elementary courses in general feeding, but will also be valuable to the farmer who has not had a technical education in agriculture. Thus it has been deemed wise to omit many minor details and a large part of the mass of experimental data from which the general conclusions are deduced."

*Principles of Feeding Farm Animals* contains 21 chapters, an appendix, and an index. The titles of the several chapters follow: The Chemical Composition of Feedingstuffs; The Chemical Composition of Farm Animals; The Digestion of the Nutrients; The Digestibility of Feedingstuffs; Functions of the Feed Nutrients in the Animal Body; Energy in Feedingstuffs and its Uses in the Animal Body; The Compounding of Rations; The Feed Requirements of Farm Animals; Grains and Seeds; The Cereal By-Products; The Oil By-Products; The Packinghouse By-Products; Miscellaneous Concentrates; The Hays; Fodders and Stovers; The Straws; Pasture Crops; Silage; Miscellaneous Roughages; Factors Affecting the Utilization of Rations; and The Fertilizing Values of Feedingstuffs.

*The Flow of Homogeneous Fluids Through Porous Media.* By M. MUSKAT. McGraw-Hill Book Company, New York and London, 1937. Pp. xix 763, figs. 284. Price \$8.

To say the least, this book represents a very ambitious undertaking. Its method of approach opens broad vistas on major physical and economic questions. The scope of the work is well indicated in the introduction, prepared by R. D. Wyckoff. He says:

The subject matter of this treatise, the flow of homogeneous fluids through porous media, while distinctly limited by the qualifications "homogeneous" and "porous," is nevertheless sufficiently wide in scope to find application in many branches of applied science. In such fields as ground-water hydrology, encompassing the provision and maintenance of water supplies, irrigation, and drainage problems, and petroleum engineering, involving the production of gas and oil from their underground reservoirs, the applications are evidently of basic importance. Equally important are applications to specific problems encountered in civil engineering, agricultural engineering, and many industries. Thus the diffusion and flow of fluids through ceramic materials as bricks and porous earthenware has long been a problem in the ceramic industry, and the flow of gas through molding sand a problem of the foundry. The construction of filter beds for municipal water systems and the question of water seepage through, around, and beneath dams, earthen reservoirs, and the like, have been important phases of civil engineering for which satisfactory discussions have been available only within the last few years. The scientific treatment of the problems of irrigation, soil erosion, and tile drainage, although still open to further development, can be considered already as a well-established branch of the general theory of the flow of fluids through porous media. The draining of artesian basins by deep wells or of rivers and canals by wells contiguous thereto is a problem in the flow of liquids through porous rocks or sands, as is the general subject of ground-water hydrology. And, of course, the whole physical problem of the production of oil and gas from underground sources is nothing more than that of fluid flow through porous media.

The book is made up of a preface, four parts, six appendixes, and author and subject indexes. The four parts deal, respectively, with: Foundations; Steady-State Flow of Liquids; The Nonsteady-State Flow of Liquids; and The Flow of Gases Through Porous Media. There are, in all, eleven chapters in the book, which are made up of numerous subdivisions.

The author is to be commended for having produced a scholarly treatise of far-reaching significance. Geologists, engineers, economists, manufacturers, and business executives will—directly or indirectly—derive benefit from this work. It should find a place on the reference shelf of every modern library.

*Parkways and Land Values.* By JOHN NOLEN AND HENRY V. HUBBARD. Harvard University Press, Cambridge, Mass., 1937. Pp. xiv + 135, figs. 23, plates 11, tables 12. Price \$1.50.

The preface, prepared by Henry Vincent Hubbard, indicates the thoughts that guided the authors in the preparation of this book. The following may be quoted:

In 1930 Mr. John Nolen and I, in the course of one of our very many discussions of planning matters, found ourselves particularly interested in the changing functions of the parkway in the regional plan, and in the wide differences which we knew to exist in its nomenclature, in evaluation of its service, and in expectation of its future benefits under modern circum-

stances. We felt that it would be well worth the effort to attempt to clarify our own thinking in these matters and to put our results at the disposal of others whose thoughts like ours needed some crystallization. We had no desire to prove one thing rather than another. We were concerned only to set down what the facts were and what conclusions, whether we liked them or not, seemed to us more or less inevitable from the facts.

The book contains five chapters, designated respectively: Possibilities or Evaluation of Benefits and Allocation of Costs; Parkways of Metropolitan Boston; Kansas City Parkways; Westchester County Parkways; and Summary and General Remarks. There are likewise two appendixes, entitled: List of More Important References; and Organizations and Persons Coöperating with the Harvard Department of Regional Planning on the Parkway Study.

The major emphasis that is now being laid on the providing of adequate recreation facilities is in keeping with some of the important trends noted by the authors. The Regional Plan Association in the New York metropolitan area has taken cognizance of some of the more significant problems involved in regional and national planning. It has been pointed out time and again by our leading planners that there should be ten acres of recreation areas for every one thousand persons living in our cities. This is aside from municipal, state, and national forests. The subject dealt with by the authors cannot be divorced from city planning, water supplies, sewage disposal, and land use in general. The broad subject of land-use planning must, of necessity, reckon with parkways and land values. This book, undoubtedly, will prove helpful to all interested in improving transportation and recreation facilities and in the betterment of esthetic and social conditions.

*Practical Methods in Biochemistry.* Second Edition. By FREDERICK C. KOCH. William Wood & Company, Baltimore, 1938. Pp. viii + 302, tables 29. Price \$2.25.

The first edition of this book appeared in 1934. It was reprinted in August, 1935, and a second edition appeared in September, 1937. It is noted by the author in the preface to the second edition that "In this revision I have eliminated some of the duplications of methods, have revised others and have added specific instructions on urea clearance and on the quantitative estimation of albumin, globulin, sodium and potassium in blood serum."

The book is made up of three parts, entitled respectively: The Chemistry of Cell Constituents; The Chemistry of the Digestive Tract; and Blood and Urine. There are 13 chapters, designated as follows: Carbohydrates; Lipins; Proteins; Nucleoproteins and Nucleic Acids; Hydrogen Ion Concentration; Salivary Digestion; Gastric Digestion; Intestinal Digestion; Bile; Blood and Hemoglobin; The Quantitative Analysis of Blood; The Quantitative Analysis of Urine; and The Chemical Examination of Urine for Pathological Conditions. There are also an appendix, alphabetical list of reagents and amounts needed per student, and an index.

It was pointed out in the preface to the first edition that the author had in

mind a manual that would be helpful to medical students. The information that had been compiled, arranged, and interpreted by the author will prove useful, however, to many other than medical students. It has distinct value as a reference as well as a text book.

*Man, Bread and Destiny.* By C. C. FURNAS AND S. M. FURNAS. The Williams & Wilkins Company, Baltimore, 1937. Pp. xix + 364. Price \$3.

The authors must have felt some satisfaction in the inscription which they offer, namely: "To our respective fathers who might still be alive if nutritional knowledge had been complete during their lifetimes." Perhaps this is more than a pious wish. Be it as it may, many persons have died before their time because they did not eat enough, or because they ate too much, or because they ate the wrong things.

No one will quarrel with the authors because they have entitled their introductory statement "A Man Must Eat." In fact, most men and women—to say nothing of children—like to eat. Science and technology have helped us to produce more and better food, and have, likewise, pointed out to us the pitfalls of malnutrition.

The contents of the book are divided into seven parts and a total of 20 chapters. These are followed by an appendix, notes, and an index. The several parts and chapters are designated as follows: Part One—Historical: The Savage Brute, and Early Ramblings in Nutrition; Part Two—The Power House: Energy, and Quantity; Part Three—Essential Fuel: The Big Three, Minerals, and Vitamins; Part Four—Good Food—Good Health: Jackstraws, Decaying Teeth Through the Ages, Diet and Mentality, Stamina, and Gullible's Travels; Part Five—Come and Get It: On Dining Well, Going Through the Mill, Germs vs. Eating, What Cooks Forget, and Cook Book Review; Part Six—Economic Aspects: The Eating World, and Filling the Pantry; Part Seven—The Future of Food: Helping Nature.

By the designation used, the authors make it clear to the reader that the book is intended to make a strong popular appeal. They have succeeded in showing that food is a source of energy—raw material for the building of animal tissues and a vital part of our whole political, economic, and social structure. Teachers, dieticians, home demonstration agents, and well-informed men and women, in general, will find in this book concrete information and helpful suggestions.

*Mother Earth.* By GILBERT WOODING ROBINSON. Thomas Murby & Co., London, 1937. Pp. viii + 202, maps 2, figs. 6, plates 1. Price 5/6 net.

This little book is full of stimulating thought. The author has tried to grasp the fundamental relations and significance of land-use factors in the unfolding of human history. As populations grow or decline, as individuals and groups move from region to region, land and soil factors somehow make

themselves felt. In this connection, the statement addressed to the general reader by the author may be quoted:

I have addressed these Letters on Soil to an old friend and colleague who is probably better known to the public than I am. Although he may not agree with all that has been written herein, I know he will read them with attention, because they are about the Soil, which is the Land. And because so many have read what he has written about the land, I dare to hope that some may read these letters with interest, for they deal with matters on which we ought to think rightly. The affairs of the soil may not have the strange magnificence of the outer universe or the curiosity of the inner recesses of the moon; but they touch our daily lives more intimately. So I commend them to your notice and ask your indulgence for the homeliness of my story.

We may also note the following quotation from St. Francis of Assisi:

Praised be, my Lord, for our sister, Mother Earth, which doth sustain and keep us, and bringeth forth divers fruits, and flowers of many colours, and grass.

The book contains 17 chapters, designated as follows: Introductory; Soil or A Soil; Soil Material; Humus; Structure and Tilth; The Soil Profile; Some Typical Soils; Soil Moisture; Soil Fertility; Manures and Fertilizers; Lime; Soil Surveys; Arable, Grass and Forest; Our Agricultural Soils; Waste Lands; *Corruptio Optimi Pessima*; and Concluding Reflections.

Finally, we may note the concluding paragraph by Doctor Robinson. It may have been written from the point of view of the British Isles. None the less, the statement has very general application:

Viewing the future of the soils of the world and realizing that their resources for food production are more limited than was formerly supposed, I cannot avoid the conclusion that our own soil must bear a larger share in the provision of our food. The present campaign for raising the level of fertility of our soil has originated under the threat of war. It is no less necessary if we remain at peace. I believe that the solution of the problem will be found, not in the adoption of revolutionary and artificial methods, but in the enlightened yet conservative use of our natural resources of soil and climate, with Science always the servant but never the master.

*Theory and Practice in the Use of Fertilizers.* Second Edition. By FIRMAN E. BEAR. John Wiley & Sons, Inc., New York, 1938. Pp. ix + 360, figs. 63, tables 71.

The first edition of this book appeared in 1929. It found ready use in many classrooms. The second edition brings up to date some of the newer trends and developments in the field of fertilizer manufacture and practice. In the preface to the second edition, the author notes:

Progress in the manufacture and use of fertilizers has been very rapid during the period that has elapsed since the first edition of this book was published. Accordingly, it became necessary to make a number of changes throughout the text, to rewrite several chapters entirely, and to add a chapter on "trace" elements. It is hoped that, with these changes, the book may continue to serve a useful purpose to those interested in the growing of higher acre yields of the standard crops.



The 20 chapters and the index which make up the book do not, generally speaking, differ greatly from the make-up of the first edition. As the author points out, however, the second edition contains one more chapter than the first edition. This has to do with *trace* elements in soils and crops.

The student of soils, the agronomist, and the progressive farmer may depend on this book for factual information developed by the American experiment stations. Fertilizer materials have changed in character, as has soil management from the point of view of fertilizer practice. Among the newer developments in the manufacture and use of commercial fertilizers, mention may be made of fertilizer placement experiments and the addition to mixed fertilizers of small quantities of so-called *trace* elements. Altogether, the newer processes of fertilizer manufacture, the newer types of fertilizer materials on the market, and the newer methods of applying fertilizer are all widely understood. The author takes cognizance of all of these changes in the manufacture and use of commercial fertilizers.

*Knowing Your Trees.* By C. H. COLLINGWOOD. The American Forestry Association, Washington, D. C., 1937. Pp. 109, illus. 246.

The American Forestry Association, under whose auspices this book was published, has placed under debt to itself a great number of intelligent and public-spirited persons. It has helped to visualize the meaning of trees and forests in our national economy.

This volume contains a foreword, 50 chapters dealing with individual species and varieties of trees, and an index.

The why of this book is indicated in the foreword. The following may be quoted:

This book—"Knowing your Trees,"—is a response to this public demand for the first fifty tree descriptions which have appeared in American Forests, with all statistical data brought up to the latest available figures. Similar descriptions of other native or adopted trees will continue to appear in the magazine from month to month until all trees familiar to the American landscape have been presented. From time to time these will also be assembled in book form.

Aside from the helpful information contained in the text, the numerous and fine illustrations should receive special commendation. Both the student and the general reader will find much satisfaction in adding this book to their reference shelves.

JACOB G. LIPMAN

# CATION EQUILIBRIA IN PLANTS IN RELATION TO THE SOIL

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Fundamental investigation of cation equilibria in the plant in relation to the composition of the soil must be carried out in solution cultures or sand cultures in which the substrate is strictly controlled during the experiment. In applying the results of such fundamental experiments to plants grown in the soil, many difficulties are encountered (3). In working with soil solutions these difficulties are only partly solved, because the natural conditions in the soil—a soil solution in equilibrium with a solid phase—can be only partly imitated; for that purpose the addition of colloidal matter to the solution or sand culture has been tried (1, 4).

From an agricultural point of view, now that so much fundamental work on the ion uptake of plants has been done by plant physiologists, the most promising method is: first to study the plant growth and the uptake of ions under soil conditions that are as strictly defined as possible, then to correlate a large quantity of experimental data for soil and plant, and finally to try to elucidate the results on the basis of conclusions drawn from general physiological work (5).

The purpose of this paper is to offer a contribution to the study of this problem through a discussion of some pot culture experiments on soils with greatly varying amounts of added cations, both plant growth and cation content of the plants being studied.

## EXPERIMENTAL

In these experiments an attempt is made to minimize the influence of the exchangeable cations already present in the soil: *a.* by choosing acid soils with a low degree of saturation of the adsorption complex with basic ions; *b.* by adding amounts of cations large in comparison to those already present in the soil.

The advantages of this scheme are that one is as independent as possible of the original cation ratio in the soil and has the opportunity to establish new cation ratios, including extreme cases. As a basis of calculation for the cation content of the soil to be brought into relation with the uptake by the plants, the cations that were added in the form of carbonates—to effectuate exchange with the H ions of the adsorption complex—are added to the cations already present in solution and in exchangeable form, as determined by extraction of

the soil by 0.1M HCl (1:20). It is assumed that the exchangeable and dissolved cations will be available to the plant in the same way and to the same extent as are those added to the soil in the form of carbonates. This assumption is more or less arbitrary, but since we have no exact notion as to the availability of the cations in different forms in the soil, we may as well take this assumption as a working hypothesis. In all our diagrams, therefore, we plot the cation content of the plant against the total sum of the exchangeable cations present in the soil. The discussion of our first experiment, described in this paper, will serve as a good example of the principle followed in this series of experiments.

We took an acid sandy soil, rich in humus (13 per cent), with a pH in aqueous suspension of 4.3 and a total saturation capacity ( $T$ -value) of 28 m.e. in 100 gm. soil, of which 8.5 m.e. (30 per cent) was saturated by the sum of the cations Ca, Mg, K and Na. The sum of cations added, for all treatments, amounted to 7 and 14 m.e. respectively, which raised the degree of saturation theoretically to 55 and 80 per cent respectively. The amount of each of the cations present in the soil and added separately or in different combinations, is given in table 1, in which the complete data on this experiment are brought together.

The experiment was carried out with two parallel series in Mitscherlich culture vessels containing about 5 kgm. of air-dried soil. After the carbonates were thoroughly mixed with the soil, a hundred seeds per pot of "Westerwoldsch raaigras" (*Lolium italicum westerwoldicum*), a very productive Dutch strain of Italian rye grass, were sown on April 9, 1934. As a basal dressing, each pot received 1.17 gm. of secondary ammonium phosphate (about 80 kgm. N and 200 kgm.  $P_2O_5$  per hectare). The soil was maintained throughout the experiment at a water capacity of about 50 per cent of the maximal.

After coming up on April 17, the grass showed such a vigorous growth that a first cut could be taken on May 16; a second cut was taken on June 8 but not studied further, as the aftergrowth had been irregular because of the great differences in yield of the first cut.

From the first two columns of table 1, we see that the cations were given separately in single and double amount and also combined in pairs in half and single amount; four pots received further combinations of Mg, K, and Na and of all four cations together.

In the next five columns of table 1 are shown the amounts of cations present in 100 gm. of soil after the addition of the carbonates. Calcium occurred in the soil in an amount about equal to that of the single addition of carbonate, but the single and double applications of the other cations are very large in comparison with the amounts present in exchangeable state in the original soil. We added such large quantities, not only to be independent of the cation ratio in the original soil, as has been stated, but also to alter the degree of saturation of the adsorption complex with Mg, K, and Na in a manner similar to that in

TABLE 1

*Soil values and yield and cation content of Italian rye grass in a pot experiment*

TREATMENT		CATIONS					pH OF THE SOIL, END OF EXPERIMENT	YIELD OF GRASS*	CATIONS PRESENT IN 100 GM. GRASS*					
		Added in the form of carbonate	Present in 100 gm. soil						Ca	Mg	Na	K	Sum	
			Ca	Mg	Na	K								Sum
m.e.	m.e.	m.e.	m.e.	m.e.	gm.	m.e.	m.e.	m.e.	m.e.	m.e.				
0	0	6.7	1.1	0.3	0.4	8.5	4.8	9.8	17	24	11.5	133.5	186	
1 Ca	7	13.7	1.1	0.3	0.4	15.5	6.0	8.5	35.5	26.5	12.5	129	203.5	
2 Ca	14	20.7	1.1	0.3	0.4	22.5	6.6	5.0	39	25.5	12	124	200.5	
1 Mg	7	6.7	8.1	0.3	0.4	15.5	5.6	8.0	14	49	9.5	123	195.5	
2 Mg	14	6.7	15.1	0.3	0.4	22.5	6.7	7.8	11.5	62.5	9	112	195	
1 Na	7	6.7	1.1	7.3	0.4	15.5	6.4	5.8	8	17.5	97	78.5	201	
2 Na	14	6.7	1.1	14.3	0.4	22.5	7.4	...	...	...	...	...	...	
1 K	7	6.7	1.1	0.3	7.4	15.5	6.5	5.5	8	17.5	13	169	207.5	
2 K	14	6.7	1.1	0.3	14.4	22.5	7.3	...	...	...	...	...	...	
$\frac{1}{2}$ Ca + $\frac{1}{2}$ Mg	7	10.2	4.6	0.3	0.4	15.5	5.8	7.3	23	36	15	123	197	
1 Ca + 1 Mg	14	13.7	8.1	0.3	0.4	22.5	6.5	7.0	24.5	47	10.5	130.5	212.5	
$\frac{1}{2}$ Ca + $\frac{1}{2}$ Na	7	10.2	1.1	3.8	0.4	15.5	6.1	10.5	18	22.5	61.5	103	205	
1 Ca + 1 Na	14	13.7	1.1	7.3	0.4	22.5	7.2	8.0	13	22	93.5	78.5	207	
$\frac{1}{2}$ Ca + $\frac{1}{2}$ K	7	10.2	1.1	0.3	3.9	15.5	6.2	6.0	14.5	20.5	8	159	202.5	
1 Ca + 1 K	14	13.7	1.1	0.3	7.4	22.5	7.1	6.0	11	18.5	6	163	198.5	
$\frac{1}{2}$ Mg + $\frac{1}{2}$ Na	7	6.7	4.6	3.8	0.4	15.5	6.2	7.3	10.5	31.5	58.5	99	199.5	
1 Mg + 1 Na	14	6.7	8.1	7.3	0.4	22.5	7.0	5.8	7	27.5	88.5	72	195	
$\frac{1}{2}$ Mg + $\frac{1}{2}$ K	7	6.7	4.6	7.3	3.9	15.5	6.2	11.0	10.5	29	16.5	159	215	
1 Mg + 1 K	14	6.7	8.1	7.3	7.4	22.5	7.2	5.0	6	23.5	7	152	188.5	
$\frac{1}{2}$ Na + $\frac{1}{2}$ K	7	6.7	8.1	3.8	3.9	15.5	6.6	5.8	6.5	18.5	35	122.5	182.5	
1 Na + 1 K	14	6.7	8.1	7.3	7.4	22.5	7.3	...	...	...	...	...	...	
$\frac{1}{2}$ Mg + $\frac{1}{2}$ Na + $\frac{1}{2}$ K	7	6.7	3.43	2.63	2.73	15.5	6.2	9.8	9.5	27	31.5	137	205.5	
$\frac{2}{3}$ Mg + $\frac{1}{3}$ Na + $\frac{1}{3}$ K	14	6.7	5.76	4.96	5.06	22.5	7.2	6.3	4.5	22	33	133	192.5	
$\frac{1}{2}$ Ca + $\frac{1}{2}$ Mg + $\frac{1}{2}$ Na + $\frac{1}{2}$ K	7	8.45	2.85	2.05	2.15	15.5	6.4	9.3	13	24	18.5	148.5	204	
$\frac{2}{3}$ Ca + $\frac{1}{3}$ Mg + $\frac{1}{3}$ Na + $\frac{1}{3}$ K	14	10.2	4.6	3.8	3.9	22.5	7.1	8.3	8	24	27.5	139.5	199	

\* Dry matter of first cutting.

ordinary practice for Ca, when such an acid soil is limed with fairly large amounts of calcium carbonate.

† The pH values of the soil, given in the next column of table 1, were determined at the end of the experiment. The pH of the original soil was 4.3 at

the beginning of the experiment and 4.8 afterward. Compared with this latter value, the single amount of calcium and magnesium carbonate raised the pH, on the average, 1.0 unit, the double amount, 1.8; the single amount of potassium and sodium, raised the pH 1.7 units, the double amounts, 2.6.

It was to be expected that the large quantity of cations, especially of K and Na would cause serious disturbances of the growth. In three pots; namely, those receiving 2 K, 2 Na, and 1 K + 1 Na, the plants showed a very poor growth from the beginning and were almost completely destroyed before the first cutting. The plants from the pots receiving single additions of K and Na, separately and in combination, also showed a poor growth, as will be seen from the yields listed in table 1. In general, the yields from pots with double amounts of carbonate are less than those from pots with single quantities, and the latter are somewhat lower than the yield from the untreated pot, with three exceptions.

#### DISCUSSION

Table 1 shows that the additions of cations to the soil cause very considerable variations in the Ca, Mg, Na, and K content of the plants. Notwithstanding these large variations for the single ions, the sum of the four cations remains approximately constant, ranging from 182.5 to 215 m.e., 14 of the 22 values lying between 195 and 205 m.e. We may conclude, therefore, that in this experiment the mutual replacement<sup>1</sup> of the cations in the plant was nearly equivalent.

A better impression of the changes in composition of the plants can be obtained from figures 1-3, in which the amount of the four cations in the plants are plotted against the cation concentrations in the soil, as mentioned in table 1. In each diagram the values for the check and for the single, and the double addition (indicated by overlining), when present, are connected by a line; the points for the other pots are indicated as far as possible.

From figure 1 we see that the amount of calcium in the plant is doubled when a single amount of calcium carbonate is added; the double application gives only a small additional rise. The addition of magnesium in addition to calcium distinctly lowers the Ca uptake, whereas Na and K additions and all combinations containing these ions, with or without calcium, lower the calcium content, in general, to values below the value of the check.

From figure 2 we see that the check plants contain more magnesium than calcium; the rise as a result of the application of single or double quantities of Mg is also greater than that for calcium. In contrast with the influence of magnesium on calcium, Ca application does not distinctly lower the Mg content. The effect of sodium and potassium on magnesium shows the same course as that on calcium, i.e., low Mg values with Na and K carbonate without Mg, somewhat higher values when the alkali ions are given together

<sup>1</sup> We prefer the term "replacement" to "antagonism," when only the phenomenon of a mutually influenced increase and decrease of different ions is meant and not a physiological or a toxic effect on the plant.

with magnesium in small quantities, and again lower values for the treatments 1 Mg + 1 Na and 1 Mg + 1 K. For both calcium and magnesium, we find a greater depression from applications of K than from those of Na.

Figure 3 gives a totally different aspect for the Na uptake. All treatments without sodium show low Na values in the plant, without regular differences;

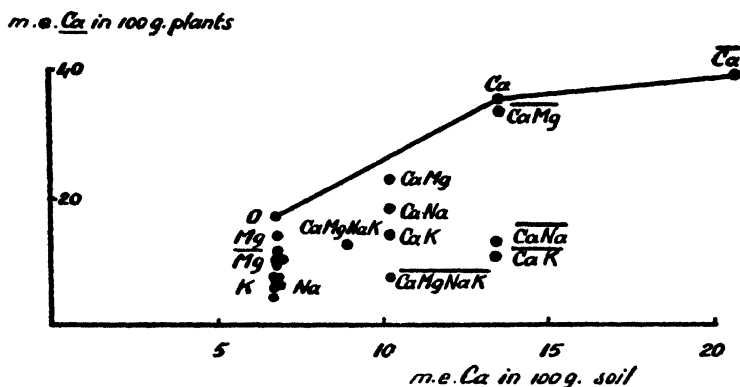


FIG. 1. RELATION BETWEEN EXCHANGEABLE CALCIUM IN THE SOIL AND ITS CONCENTRATION IN THE PLANT

The treatments containing double amounts of cations are overlined in all figures in this paper

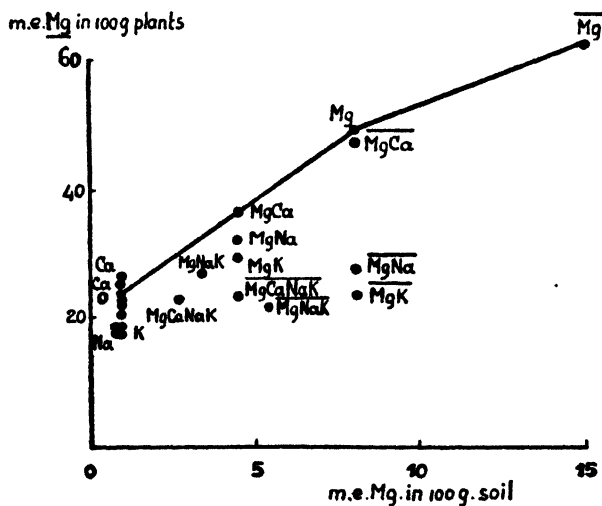


FIG. 2. RELATION BETWEEN EXCHANGEABLE MAGNESIUM IN THE SOIL AND ITS CONCENTRATION IN THE PLANT

Na application, however, raises the Na content to very high values. The depressions caused by additional Ca and Mg applications are visible, but of little importance; all combinations of potassium and sodium give a very considerable lowering of the Na content in comparison with sodium application

without potassium. We get the impression, from the values for the combinations containing smaller amounts of sodium, that the Na line is slightly curved; this is true also for the K line.

For potassium, figure 3 again shows quite another aspect. Potassium in the plant is high for the check, as the untreated soil is not very deficient in K; the single K application produces a still higher value, although this increase in K uptake is proportionally much smaller than the increases in the corresponding

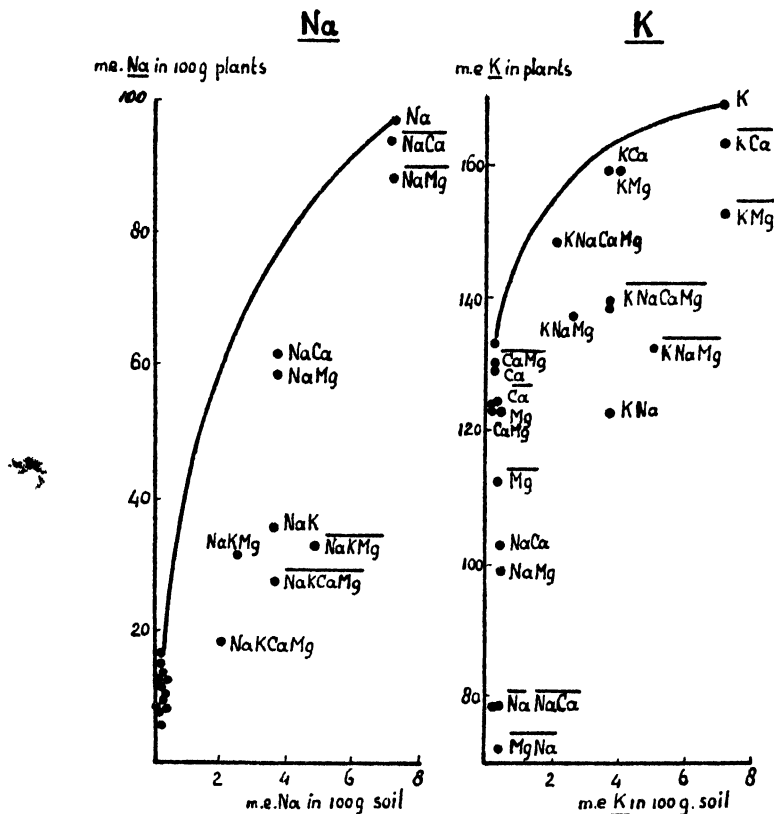


FIG. 3. RELATION BETWEEN EXCHANGEABLE SODIUM AND POTASSIUM IN THE SOIL AND THEIR CONCENTRATIONS IN THE PLANT

cases for Ca, Mg, and Na. The Ca treatments, with or without potassium, give K values that do not deviate greatly from the curve; in all cases magnesium distinctly lowers the K values, if compared with the treatments without Mg. The greatest depression of the K content is found, however, with Na application, alone or combined with calcium and magnesium. Without potassium addition, we find in these cases very low K values for plants; when equal K and Na are applied, potassium is held more or less in equilibrium when com-

pared with the uptake from the original soil; with greater additions, however, the K content is again lowered.

In comparing the amount of each ion in the plant for the pot treatment in which the particular ion is present in exchangeable form in the soil in amounts of 6.7 to 8.1 m.e., we see that potassium is the most readily absorbed; sodium, magnesium, and calcium then follow successively, a sequence which has been observed in many other investigations including solution-culture experiments. As we find almost equivalent replacement of one ion by the others, it is clear that application of the ion that is taken up most easily, namely, K, will exert the greatest depressive action on the other ions. This fact can be clearly seen in the graphs for Ca, Mg, and Na. A decrease in the depressive action of the Na, Mg, and Ca ion is visible for each of these ions respectively in three of the four diagrams.

Under normal conditions, we find in all soils, at least under our climatic conditions, a great excess of exchangeable calcium as compared with the other basic ions, whereas the amount of magnesium usually exceeds that of potassium and sodium. In many soils the excess of Ca is much greater than that in the soil with a low degree of saturation used in this experiment. It will be clear that the changes in the cation uptake, caused by the different ion applications, are controlled to a considerable extent by the original cation ratio, although our additions, at least of K and Na, are so large that the amounts of these ions present in the original soil, can almost be neglected. Exchangeable sodium and potassium, for instance, are present in the soil in almost equal amounts; this K-Na ratio is sufficient for an abundant K uptake, whereas it results in only a very small Na uptake. If, then, we add potassium alone or in combination with calcium and magnesium, the K in the plant increases considerably and replaces part of the Ca and Mg, the Na content being already so low that no appreciable further decrease takes place. If, however, sodium alone or combined with calcium and magnesium is added, the originally low Na value rises much more than potassium did in the former case; but in this instance not only calcium and magnesium but, above all, the high content of K is lowered by replacement because of the important Na uptake. Thus an equal addition of both alkali ions causes a much greater change in the conditions for uptake of sodium than for potassium, because from the original soil a large amount of K, but only a small amount of Na, has already been taken up.

In a similar way, we can compare the Ca and Mg uptake. Calcium added in an amount about equal to the excess already present in the soil and taken up with the greatest difficulty by the plant, does not cause great variations in the composition of the plant and therefore does not play an important part in ion replacement. The same amount of magnesium, added to the soil containing only relatively little Mg, naturally causes a greater change in the ratio of magnesium to the other ions and has, therefore, a greater influence on the com-



position of the plants, because from an equal application more magnesium than calcium is taken up.

In reviewing the results of this experiment, it is evident that, generally, the uptake of a cation cannot be brought into simple relation with the concentration of that ion in the soil in any form, but that it must be regarded as dependent upon the ratio of that ion to the others in the soil. Other influences, for example, that of the anions on the cation uptake, need not to be discussed here, because these have been ruled out in this experiment. It may perhaps seem strange that, in fertilizing experiments, the ion concentration in the soil should not be the principal factor controlling the ion uptake, but one must bear in mind that in ordinary experiments, as a rule, only the concentration of the particular ion being studied is changed; the ratio of the other ions remains the same and need not to be taken into consideration. If, however, we compare crops grown on soils with greatly differing cation ratios, we may conclude that in such cases these ratios will certainly be of special importance.

When not only the concentration of the ion studied, but also that of the other cations in their ratio to that ion, is involved, it will, of course, be much more difficult to find a satisfactory relation between soil values and ion uptake. Burström (2) was the first to study quantitatively in solution cultures the uptake of one ion, when the concentration of another anion was varied and the concentration of the ion studied remained constant. The results of his experiments can not, as yet, be applied to soil conditions. Our experiments, however, with more or less extreme conditions as regards the cation ratio, gave us the opportunity to study this complicated relationship between the ion uptake and the variations in the amounts of all four cations in the soil. We did not intend to establish exact rules about this relationship, but only tried to find, for each ion separately, a value in the soil which would be more closely related to the composition of the plant than the simple concentration value plotted on the abscissa in figures 1-3.

One of the ways of taking all ions into account is by expressing the cations in the soil in percentages of the sum of Ca, Mg, Na, and K, because, in so doing, the addition of one cation always affects the percentage figure of all four. When expressing the amount of cation in percentage figures, we make no allowance, however, for the great differences in the influences of each cation on the others. It will be evident that these differences can be brought into consideration by giving to each ion a special coefficient, with which its concentration in the soil must be multiplied before it is brought into relation with the concentrations of the other ions.

Taking also into consideration the figures obtained in other experiments on different sandy soils, we worked out for the present experiment the following coefficients, which gave the best correlation for each ion with the values found in the plants: Ca, 1; Mg, 2; Na, 10; K, 20.

Using these coefficients, we established the following relationships for the values in the soil, to be correlated with the cation uptake by the plants:

$$\text{For Ca: } \frac{\text{Ca}}{0.2 \text{ Mg} + \text{Na} + 2 \text{ K}}$$

$$\text{For Mg: } \frac{2 \text{ Mg}}{0.1 \text{ Ca} + \text{Na} + 2 \text{ K}}$$

$$\text{For Na: } \frac{10 \text{ Na}}{0.1 \text{ Ca} + 0.2 \text{ Mg} + 2 \text{ K}}$$

$$\text{For K: } \frac{20 \text{ K}}{0.1 \text{ Ca} + 0.2 \text{ Mg} + \text{Na}}$$

To obtain figures that are more convenient for use, the decimals in numerator and denominator are chosen differently. We do not claim that the for-

TABLE 2  
*Values of magnesium obtained by formula*

TREATMENT	MAGNESIUM PRESENT IN THE SOIL			Mg IN PLANTS, M.E. PER 100 GM. DRY MATTER
	In m.e. per 100 gm.	In per cent of sum	Determined by the formula	
0	1.1	13	1.18	24
1 Ca	1.1	7	0.80	26.5
1 Na	1.1	7	0.24	17.5
1 K	1.1	7	0.14	17.5
1 Mg	8.1	52	8.70	49
1 Mg + 1 Ca	8.1	29.5	5.86	47
1 Mg + 1 Na	8.1	29.5	1.82	27.5
1 Mg + 1 K	8.1	29.5	1.02	23.5

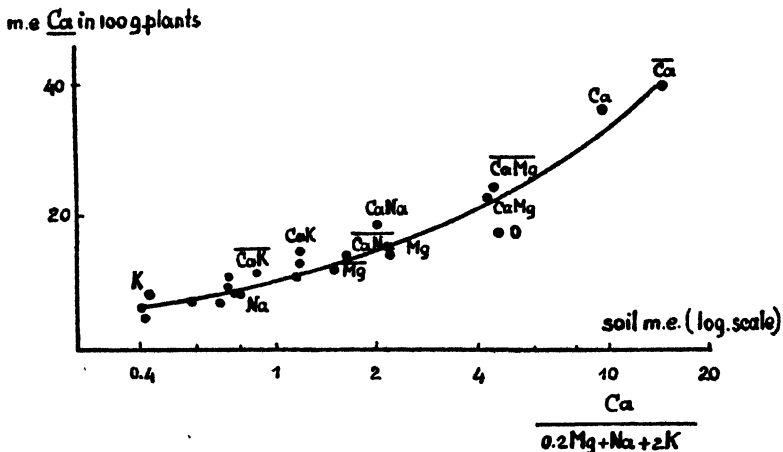


FIG. 4. RELATION BETWEEN THE SOIL VALUE FOR EXCHANGEABLE CALCIUM, CALCULATED BY THE GIVEN FORMULA, AND THE CONCENTRATION IN THE PLANT

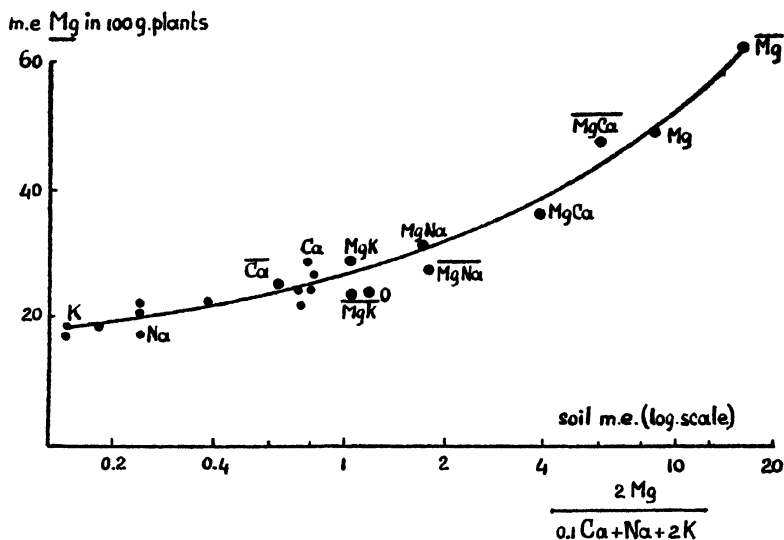


FIG. 5. RELATION BETWEEN THE SOIL VALUE FOR EXCHANGEABLE MAGNESIUM, CALCULATED BY THE GIVEN FORMULA, AND THE CONCENTRATION IN THE PLANT

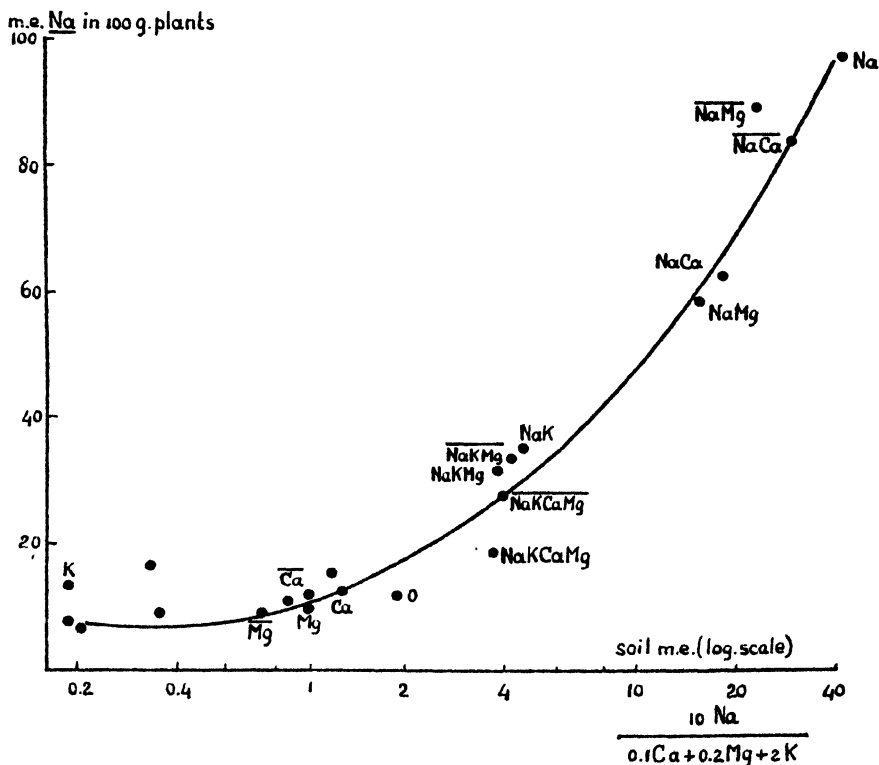


FIG. 6. RELATION BETWEEN THE SOIL VALUE FOR EXCHANGEABLE SODIUM, CALCULATED BY THE GIVEN FORMULA, AND THE CONCENTRATION IN THE PLANT

mulas given are the best for correlating the relations in the soil with those in the plants; they are meant only to indicate the order of magnitude with which each ion will affect its own uptake and that of the other three cations. In table 2 are given, as an example of some values obtained according to these formulas, the figures for eight treatments with magnesium in comparison with the Mg values from table 1 and when expressed in percentages of the four cations in the soil.

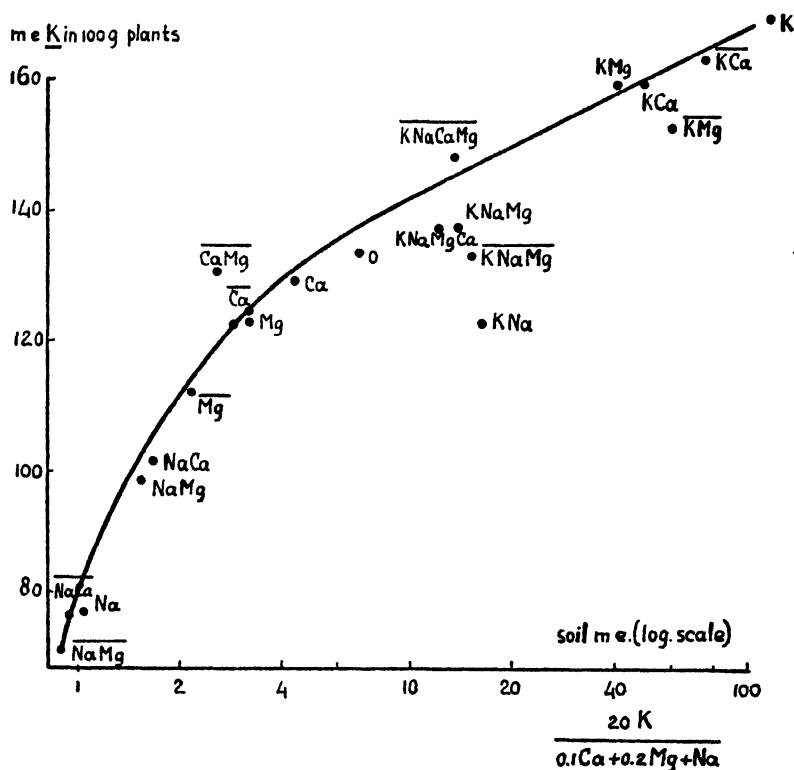


FIG. 7. RELATION BETWEEN THE SOIL VALUE FOR EXCHANGEABLE POTASSIUM, CALCULATED BY THE GIVEN FORMULA, AND THE CONCENTRATION IN THE PLANT

As can be easily seen from table 2, Mg in the plants correlates much better with the Mg values in the soil determined by our formula, than with those of the other columns. In figures 4-7 are plotted, for each cation separately, the soil values according to our formulas, for all treatments, against the ions in the plants, as was also done in the former diagrams. Because 17 of the 22 treatments for all ions gave soil values lying in the lowest sixth part of the scale, these values are plotted logarithmically, so as to bring out more clearly the position of the single points on the graphs.

These figures show that, with a few exceptions, there is a fairly close rela-

tionship between the soil values and those of the plants; this is shown by average curves. It is distinctly seen that, by giving to potassium 20 times, to sodium 10 times, and to magnesium twice the value of calcium, the values with Mg, Na, and K in the denominator are transferred in increasing measure to the left in the diagrams. The soil values fit to the curves much better than they do in figures 1-3.

The possible importance of using such formulas to establish a useful relationship between soil and plant values will be discussed on another occasion, when we hope to give more experimental facts about this subject. The conclusion to be drawn at present is that it seems possible to set up such a relationship, which we hope may be of some assistance in elucidating the complicated process of ion uptake from a soil.

#### SUMMARY

An experiment is described in which great changes in the ratio of Ca, Mg, K, and Na in a soil relatively poor in exchangeable cations are effected by the addition of large quantities of carbonates of these ions. The amount of cations in Italian rye grass, grown in pots on samples of this soil, supplied with different amounts of these cations, was studied. As was to be expected, great changes in plant composition were found under the influence of the varying ratio in the soil. The well-known mutual replacement of the cations in the plant took place in this experiment, for the most part, in nearly equivalent amounts, the uptake and the replacement value being largest for potassium and decreasing progressively for sodium, magnesium, and calcium. In consequence of this different replacement capacity of the four cations, one finds no satisfactory relationship between the concentration of an ion in the soil and that in the plant, even when concentration in the soil is expressed in percentage figures. By giving, however, to the concentration figure of each cation in the soil a special coefficient and taking the ratio of the soluble plus exchangeable amount of each ion and the same amount of the others, we obtained soil values which gave a satisfactory correlation with the composition of the plants. In a further paper, additional experimental results will be given, on its basis of this method of expressing the cation concentrations in the soil.

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# FERTILIZATION IN ITS RELATIONSHIP TO THE COURSE OF NUTRIENT ABSORPTION BY PLANTS<sup>1</sup>

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## INTRODUCTION

It is self-evident that, other things being equal, fertilizer needs increase with added nutrient needs of plants. The equality of these other factors, however, is easily deranged by the inherent thriftiness of the plants and their ability to extract nutrients from naturally occurring sources; the equally inherent distribution of the nutrient needs; and the reaction of the plants to modifications in soil conditions brought about by the various ingredients in the fertilizer. Thus the relationships between nutrient and fertilizer needs are, by no means, necessarily parallel. The purpose of this article is to delineate, on the basis of the aforementioned factors, the significance of nutrient needs and their distribution during the life of the plant, to the use of fertilizers.

It cannot be assumed that the nutrient needs of plants are the same as the nutrient contents of plants, for the following reasons:

Nutrient absorption varies with supply between two limiting values, one of which represents luxury consumption, the other a physiologically insufficient but not growth-inhibiting minimum.

An undetermined portion of substances absorbed during growth returns to the soil long before maturity, by root excretions or remigration, cuticular sloughing of living plant parts, and decay and lixiviation of dead parts.

The unharvested parts of plants contain nutrients which are not removed in the harvest.

If based on sufficiently numerous and reliable observations, however, nutrient contents afford an approximation of the nutrient needs of the species. In view of the great variation involved, certainly no more than an approximation of nutrient needs is to be obtained in this way, and for practical purposes of fertilization, anything more is not absolutely necessary. With a given need, the distribution over a period of time, or the course of nutrient absorption, is very much of a factor in determining fertilizer requirements. No sensible physiologist would deduce rules for the form of the daily fare from the fact that man in the course of 70 years requires  $x$  million calories in nutrition. The applicability of the rules assumes, among other things, adaptation of the supply to age, sex, type of work, climate, and other factors of life. Relatively,

<sup>1</sup> Translated from the German, by J. D. Romaine, chief agronomist, American Potash Institute, Inc., Washington, D. C.

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the same thing holds true for plants. Nutrients must be not only sufficient for plants but also available at the right time. Such considerations have engendered numerous investigations on the course of nutrient absorption by plants.

#### LIEBSCHER'S TEACHINGS

In Germany, Liebscher was the first to draw attention to this question by a study published in 1887 (2). His conclusions may well be quoted herewith:

In a comparison of the curves of organic matter with those of nutrient absorption [Liebscher plotted curves in his work on the course of nutrient absorption] we see very clearly in virtually every case, that

(a) A relatively great increase in nutrient absorption during the young growing period of the plant indicates the necessity for supplying these nutrients in the readily soluble form of commercial fertilizers (grains, rape, etc.).

(b) The steeper the rise of the curve for organic matter during the time of high nutrient needs, the greater is the need for the fertilizer roughly indicated under (a) above (barley, oats or horse beans, lupine).

(c) Insignificant variability or approximate parallelism in the curves for organic matter and nutrient absorption indicates that the plants are dependent on the nutrients gradually going into solution. These nutrients are present in the soil as slowly decomposing residues from previous fertilization (clovers), or as nitrogen gradually added to the soil from the atmosphere (clovers and legumes).

(d) A relatively steep increase of the nutrient curve toward the end of the growing period (potatoes, rutabagas, legumes) or an increased nutrient need which occurs in the middle of summer after a rather long period of slow growth, and thus at the time when reactions in the soil are very strong, is an indication that fertilization with barnyard manure, which decomposes slowly, is suitable for such plants (corn, sugar beets, legumes, cabbage, chicory).

#### LIEBSCHER'S TEACHINGS IN A CRITICAL LIGHT

Sickness and death (in 1896) terminated the work of Liebscher so early that he was not able to elaborate on his theory. Succeeding work participated in by the author, first as a pupil of Liebscher and later independently, furnished abundant detailed material for a critical examination of the problem. Unfortunately, however, this examination has long been postponed. The author explained the principles first in 1926 (1, 4, 5). Those statements are still valid but require supplementing on some points. It is sought, in the following sections, to reconcile these statements to present-day views.

#### *Nutrient absorption during growth of plants*

Observations on rye, which, as the most widespread field crop, is very frequently investigated in Germany, may serve as the starting point in the study of nutrient absorption during the growth of the plant. In spite of the difficulty due to their great diversity, the results of 6 experiments conducted by T. Roemer, of Halle (3), and of 18 of my own, have been reduced to a common denominator in table 1. As was to be expected, the nutrient absorption is correlated to some degree with the development of the rye. The same applies

**TABLE 1**  
*Growth and nutrient absorption of winter rye*

PERIOD OF GROWTH	DETERMINATIONS												
	Roemer						Remy				Least	Great- est	Aver- age
	1	2	3	4	5	6	1	2	3*	4*			
1. Per cent of yield (dry matter) produced													
1. Emergence to end of winter.	4	3	2	2	2	2	8	1	2	2	1	8	2.8
2. End of winter to beginning of stalk growth.	19	18	10	7	14	9	13	11	21	33	7	33	15.5
3. Beginning of stalk growth to blossoming	46	59	63	57	65	89	62	59	38	32	32	89	57.0
4. Blossoming to maturity	31	20	25	34	19	0	17	29	39	33	0	39	24.7
2. Per cent of greatest amount absorbed													
a. Nitrogen													
1. Emergence to end of winter	15	25	15	20	10	8	40	4	6	6	4	40	14.9
2. End of winter to beginning of stalk growth	37	20	45	31	24	18	19	35	19	70	18	70	31.8
3. Beginning of stalk growth to blossoming	25	35	30	28	58	74	41	44	34	17	17	74	38.6
4. Blossoming to maturity	23	20	10	21	8	0	0	17	41	7	0	41	14.7
b. Phosphoric acid													
1. Emergence to end of winter	8	8	8	8	13	8	17	2	3	3	2	17	7.8
2. End of winter to beginning of stalk growth	28	18	34	17	40	22	24	27	32	55	17	55	29.7
3. Beginning of stalk growth to blossoming	33	41	32	37	32	70	59	58	29	20	20	70	41.1
4. Blossoming to maturity	31	33	26	38	15	0	0	13	36	22	0	38	21.4
c. Potash													
1. Emergence to end of winter	10	10	7	10	9	8	12	2	3	3	2	12	7.4
2. End of winter to beginning of stalk growth	45	38	35	28	38	35	24	32	62	79	24	79	41.6
3. Beginning of stalk growth to blossoming	25	46	58	51	53	57	64	66	19	18	18	66	45.7
4. Blossoming to maturity	20	6	0	11	0	0	0	0	16	0	0	20	5.3
d. Lime (8 experiments)													
1. Emergence to end of winter	7	8	6	8	7	4	14	2			2	14	7.0
2. End of winter to beginning of stalk growth	25	22	25	20	26	18	18	24			18	26	22.3
3. Beginning of stalk growth to blossoming	44	55	59	53	52	78	68	63			44	78	59.0
4. Blossoming to maturity	24	15	10	19	15	0	0	11			0	24	11.8
e. Magnesia (2 experiments)													
1. Emergence to end of winter							15	2			2	15	8.5
2. End of winter to beginning of stalk growth							21	25			21	25	23.0
3. Beginning of stalk growth to blossoming							64	54			54	64	59.0
4. Blossoming to maturity							0	19			0	19	9.5

\* Average of 8 independent observations each.



TABLE 2  
*Relative values for barley, rye, and wheat*

PER CENT OF GREATEST AMOUNT FORMED OR ABSORBED TO	WINTER BARLEY	WINTER RYE	WINTER WHEAT	AVERAGE	PER CENT OF GREATEST AMOUNT OCCURRING IN GROWTH PERIODS	WINTER BARLEY	WINTER RYE	WINTER WHEAT	AVERAGE
<i>I. Dry matter yield</i>									
1. End of winter . . .	4	3	4	4	Emergence to end of winter .	4	3	4	4
2. Beginning of stalk growth . . . . .	20	19	19	20	End of winter to beginning of stalk growth . . . . .	16	16	15	16
3. Blossoming . . . . .	77	76	78	77	Beginning of stalk growth to blossoming . . . . .	57	57	61	58
4. Maturity . . . . .	100	100	100	100	Blossoming to maturity . . . . .	23	24	22	23
<i>II. Nitrogen</i>									
1. End of winter . . .	16	15	16	16	Emergence to end of winter .	16	15	15	16
2. Beginning of stalk growth . . . . .	43	47	43	45	End of winter to beginning of stalk growth . . . . .	27	32	27	29
3. Blossoming . . . . .	78	86	85	83	Beginning of stalk growth to blossoming . . . . .	35	39	42	38
4. Maturity . . . . .	100	100	100	100	Blossoming to maturity . . . . .	22	15	15	17
<i>III. Phosphoric acid</i>									
1. End of winter . . .	8	8	7	8	Emergence to end of winter .	8	8	7	8
2. Beginning of stalk growth . . . . .	29	37	30	32	End of winter to beginning of stalk growth . . . . .	21	29	23	24
3. Blossoming . . . . .	73	79	79	77	Beginning of stalk growth to blossoming . . . . .	44	42	49	45
4. Maturity . . . . .	100	100	100	100	Blossoming to maturity . . . . .	27	21	21	23
<i>IV. Potash</i>									
1. End of winter . . .	11	7	11	10	Emergence to end of winter .	11	7	11	10
2. Beginning of stalk growth . . . . .	45	49	43	46	End of winter to beginning of stalk growth . . . . .	34	42	32	36
3. Blossoming . . . . .	94	95	95	95	Beginning of stalk growth to blossoming . . . . .	49	46	52	49
4. Maturity . . . . .	100	100	100	100	Blossoming to maturity . . . . .	6	5	5	5
<i>V. Lime</i>									
1. End of winter . . .	12	7	13	11	Emergence to end of winter .	12	7	13	11
2. Beginning of stalk growth . . . . .	37	29	34	34	End of winter to beginning of stalk growth . . . . .	25	22	21	23
3. Blossoming . . . . .	88	88	94	90	Beginning of stalk growth to blossoming . . . . .	51	59	60	56
4. Maturity . . . . .	100	100	100	100	Blossoming to maturity . . . . .	12	12	6	10
<i>VI. Magnesia</i>									
1. End of winter . . .	4	9	6	6	Emergence to end of winter .	4	9	6	6
2. Beginning of stalk growth . . . . .	24	32	18	25	End of winter to beginning of stalk growth . . . . .	20	23	12	19
3. Blossoming . . . . .	67	91	98	85	Beginning of stalk growth to blossoming . . . . .	43	59	80	60
4. Maturity . . . . .	100	100	100	100	Blossoming to maturity . . . . .	33	10	3	15

also to winter barley and wheat, the behavior of which is disclosed by the averages given in table 2. These have been compiled from rather heterogeneous figures, and variations among them are less than those within the

TABLE 3

*Growth and nutrient absorption of small grains, potatoes, peas, and winter rape*

PLANT	PERIOD OF GROWTH	PER CENT OF MAXIMUM FORMED OR ABSORBED		REMARKS
		Dry matter	Nutrient	
I. Small grains	1. Emergence to beginning of stalk growth . . . . .	20	40	See text under this subject.
	2. Beginning of stalk growth to blossoming . . . . .	60	50	
	3. Blossoming to maturity . . . . .	20	10	
II. Potatoes	1. Emergence to beginning of blossoming . . . . .	25	50	See text under this subject.
	2. Beginning of blossoming to beginning of leaf yellowing . . . . .	75	50	
	3. Beginning of leaf yellowing to maturity . . . . .	0*	0*	
III. Peas (Early Viktoria)	1. 14 days before beginning of blossoming . . . . .	10	15	Growth rather uniform; duration of blossoming, 2 weeks, little secondary growth. Cessation of nutrient absorption about 10 days before maturity.
	2. From 1 to beginning of blossoming . . . . .	30	65	
	3. From 2 to end of blossoming . . . . .	40	15	
	4. From 3 to maturity . . . . .	20	5	
IV. Winter rape	1. To beginning of winter . . . . .	20	40	Emergence beginning September. Normal fall growth; no complete cessation of growth during mild winter.
	2. From beginning of winter to blossoming . . . . .	50	50	
	3. From blossoming to 4 weeks before maturity . . . . .	30	10	
	4. Pod formation to maturity (comprising about 4 weeks) . . . . .	0*	0*	

\* Retrogradation by lixiviation and shedding of leaves especially of lime and potash occurring in large amounts in maturing leaves.

species. Winter grains thus form a group with respect to nutrient absorption. Typical values for them are given in the last column of table 2 and are reduced to a few summarized values in table 3, I. The rounding of the absorption figures in the summary (Table 3, I), the grouping of all soil nutrients as "nu-

triment," and the omission of the data for late winter are based on the following considerations:

Rounding is intended to prevent any illusion as to the exactness of the figures and clearly to show their character as roughly supporting data.

Although uncertain, for the present at least it may be considered that the individual soil nutrients do not exhibit deviations from the total absorption.

The late winter given as the time of the first period in tables 1 and 2 does not occur at any particular period of growth and may not logically be adduced as a point of development.

Numerous references indicate that what was said for grains applies also to other plants. Since in a small space it is impossible exhaustively to evaluate the pertinent observations, only a few examples will be adduced as proof. With spring barley, oats, and wheat, the relationships are so very simple that they easily fit into the arrangement given in table 3, I. The potato, the development of which extends over varying lengths of time according to variety and is difficultly divided into sharply differentiated periods, differs considerably from the grains. The author sought to differentiate as well as possible the points of development given in table 3, II, on the basis of numerous references available to him, hoping that in this way he approached actuality. To round out the picture, peas and winter rape are given in table 3, III and IV, as examples of seed legumes and winter oleaginous crops. Unfortunately, in the case of these, it was necessary to rely only on a few individual experiments, which naturally limits the applicability of the values given. In this connection, however, small variations are of no significance, since our norms, by origin, are only arithmetical averages around which the individual cases tend to group themselves more or less as single values around the respective mean. Pending further details given the summary of this section, it may be stated here that the nutrient absorption becomes a component characteristic to some extent in the general scheme of development of the plant species, which certainly would appear more clearly if, in the experiments, only homogeneous plants had been employed.

### *Seasonal absorption of nutrients*

Since nutrient absorption of the plants is correlated with their development, which, in turn, is correlated with the season, it follows that there is a relationship between nutrient absorption and season. The calendar as a determining basis, however, has only local validity because specific periods of development fall on quite different dates, according to geographic and climatic conditions of the location; and fixed points in development, which must be ignored if periods of absorption are divided on a calendar basis, vary considerably from year to year. A calendar basis, therefore, gives less stability to data on nutrient needs than does the adaptation of the data to the general pattern of development. Only by exact identification of the stage of development on the day of the observation do determinations on the course of nutrient ab-

sorption contribute to the solution of the problem as a whole. From statements in the reports at hand, this frequently does not seem to be sufficiently recognized.

For the practical use of fertilizers, however, recommendations for certain weeks or months are properly popular. From data at hand we have, therefore, made comparative calculations of the nutrient needs for various periods of development and of season and, based on the data in table 4, summarized these results in tables 5 and 6.

TABLE 4  
*Course of growth of various plants*

I. SMALL GRAINS	DATE OF					DAYS BETWEEN					
	1	2	3	4	5	1 and 2	2 and 3	3 and 4	4 and 5	1 and 5	2 and 5
	Seeding	Emergence	Beginning of stalk growth	Blossoming	Maturity						
1. Winter barley . . . . .	9-15	9-25	4-17	5-19	6-30	10	204	32	42	288	278
2. Winter rye . . . . .	9-25	10-5	4-9	5-25	7-14	10	186	46	50	292	282
3. Winter wheat . . . . .	10-1	10-11	4-21	6-6	7-22	10	193	46	46	295	285
4. Summer barley (Hanna type) . . . . .	4-1	4-10	5-12	6-11	7-15	9	32	30	34	105	96
II. POTATOES	DATE OF					DAYS BETWEEN					
	1	2	3	4	5	1 and 2	2 and 3	3 and 4	4 and 5	1 and 5	2 and 5
	Planting	Emergence	Beginning of blossoming	First yellowing of foliage	Maturity						
5. Very early (Erstling type with pre-sprouting) . . . . .	3-20	4-10	5-20	6-25	7-10	21	40	36	15	112	91
6. Early (July type without presprouting) . . . . .	4-10	5-10	6-23	7-29	8-15	30	44	36	17	127	97
7. Medium-early (Johannssen type) . . . . .	4-15	5-15	7-5	8-15	9-15	30	51	41	31	153	123
8. Medium-late (Industrial type) . . . . .	4-20	5-20	7-15	9-5	10-15	30	56	52	45	183	153

The dependent relationship between nutrient absorption and development is evident also in a varying duration in nutrient absorption, which tends to correspond roughly with duration of growth. Table 4 gives some examples of this. Even in the narrow compass of Germany the dates of the periods of growth vary by weeks or even months, as a result of climatic conditions of the locality and seasonal weather. The data of table 4 are applicable to other

TABLE 5  
*Nutrient absorption correlated with periods of growth*

PERIOD	LENGTH OF PERIOD	ABSORPTION FOR PERIOD		
		Nitrogen	Phosphoric Acid	Potash
<i>I. Winter barley</i>				
	<i>days*</i>	<i>kgm./ha.</i>	<i>kgm./ha.</i>	<i>kgm./ha.</i>
1. Emergence to beginning of stalk growth.....	204	35.4	16.7	34.6
2. Beginning of stalk growth to blossoming.....	32	44.2	20.8	43.2
3. Blossoming to maturity.....	42	8.8	4.2	8.6
Total growing period.....	278	88.4	41.7	86.4
<i>II. Winter rye</i>				
1. Emergence to beginning of stalk growth.....	186	36.9	18.8	41.3
2. Beginning of stalk growth to blossoming.....	46	46.2	23.4	51.6
3. Blossoming to maturity.....	50	9.2	4.7	10.3
Total growing period.....	282	92.3	46.9	103.2
<i>III. Winter wheat</i>				
1. Emergence to beginning of stalk growth.....	193	37.5	17.9	36.2
2. Beginning of stalk growth to blossoming.....	46	46.8	22.4	45.2
3. Blossoming to maturity.....	46	9.4	4.5	9.0
Total growing period.....	285	93.7	44.8	90.4
<i>IV. Summer barley (Hanna type)</i>				
1. Emergence to beginning of stalk growth.....	32	30.4	15.8	29.0
2. Beginning of stalk growth to blossoming.....	30	38.1	19.7	36.3
3. Blossoming to maturity.....	34	7.6	3.9	7.2
Total growing period.....	96	76.1	39.4	72.5
<i>V. Potatoes—very early with presprouting</i>				
1. Emergence to beginning of blossoming.....	40	37.5	12.5	47.0
2. Beginning of blossoming to beginning of yellowing of foliage.....	36	112.5	37.5	141.0
3. Beginning of yellowing of foliage to maturity.....	15	0	0	0
Total growing period.....	91	150.0	50.0	188.0
<i>VI. Potatoes—early without presprouting</i>				
1. Emergence to beginning of blossoming.....	44	37.5	12.5	47.0
2. Beginning of blossoming to beginning of yellowing of foliage.....	36	112.5	37.5	141.0
3. Beginning of yellowing of foliage to maturity.....	17	0	0	0
Total growing period.....	97	150.0	50.0	188.0

\* From table 4.

TABLE 5—*Concluded*

PERIOD	LENGTH OF PERIOD	ABSORPTION FOR PERIOD		
		Nitro- gen	Phos- phoric Acid	Potash
VII. Potatoes—medium-early				
	days*	kgm./ ha.	kgm./ ha.	kgm./ ha.
1. Emergence to beginning of blossoming . . . . .	51	45.0	15.0	56.3
2. Beginning of blossoming to beginning of yellowing of foliage. . . . .	41	135.0	45.0	168.7
3. Beginning of yellowing of foliage to maturity . . . . .	31	0	0	0
Total growing period. . . . .	123	180.0	60.0	225.0
VIII. Potatoes—medium-late				
1. Emergence to beginning of blossoming . . . . .	56	49.5	16.5	62.0
2. Beginning of blossoming to beginning of yellowing of foliage . . . . .	52	148.5	49.5	186.0
3. Beginning of yellowing to maturity . . . . .	45	0	0	0
Total growing period . . . . .	153	198.0	66.0	248.0

districts only after appropriate modifications in the dates. The evaluation of the table is reserved for the summary of this section.

*Nutrient absorption as influenced by ecological factors*

In the ecology of the plant, external growth factors arising from weather, soil, and the living world surrounding the plant all exert an important physiological effect. That this effect extends to the course of nutrient absorption is self-evident because of its close relationship to growth. The analysis of the form and distribution of the active influences would require much space and would only impair the clarity of this study. We shall content ourselves, therefore, with passing references to these influences and shall consider now the matter of nutrient supply, which is particularly important in this connection.

The available observations offer sufficient evidence that nutrient supply is a determining factor in nutrient absorption and growth and in the relationships between them. It is an ecological phenomenon if plants, within certain limits determined by inherent factors, temporarily absorb, from an abundant supply of readily absorbable nutrients, more than the normal needs, for the purpose of future elaboration; or attempt to recover as much ground as possible from a belatedly supplied nutriment, following an initially scanty supply.

A marked temporary storing of absorbed nutriment, however, is always accompanied by modifications in growth. These are slight in the case of an absorption of phosphoric acid and potash well in advance of physiological

**TABLE 6**  
*Nutrient absorption correlated with calendar periods*

PERIOD*	PER CENT OF HIGHEST AMOUNT		FORMED OR ABSORBED PER MONTH		
	Dry matter	Nutrient	Nitrogen	Phosphoric Acid	Potash
<i>I. Winter barley</i>					
1. To March 31 . . . . .	12	25	22.1	10.4	21.6
2. April . . . . .	32	35	31.0	14.6	30.3
3. May . . . . .	42	35	30.9	14.6	30.2
4. June . . . . .	14	5	4.4	2.1	4.3
Total period of growth . . . . .	100	100	88.4	41.7	86.4
<i>II. Winter rye</i>					
1. To March 31 . . . . .	16	33	30.5	15.4	34.1
2. April . . . . .	31	30	27.7	14.1	31.0
3. May . . . . .	40	31	28.6	14.5	32.0
4. June . . . . .	9	4	3.7	1.9	4.1
5. July . . . . .	4	2	1.8	0.8	2.0
Total . . . . .	100	100	92.3	46.9	103.2
<i>III. Winter wheat</i>					
1. To March 31 . . . . .	13	24	22.4	10.8	21.7
2. April . . . . .	19	26	24.4	11.6	23.5
3. May . . . . .	42	34	31.9	15.2	30.7
4. June . . . . .	20	14	13.1	6.3	12.7
5. July . . . . .	6	2	1.9	0.9	1.8
Total . . . . .	100	100	93.7	44.8	90.4
<i>IV. Summer barley</i>					
1. April . . . . .	11	23	17.5	9.1	16.7
2. May . . . . .	45	47	35.8	18.5	34.1
3. June . . . . .	40	28	21.3	11.0	20.3
4. July . . . . .	4	2	1.5	0.8	1.4
Total . . . . .	100	100	76.1	39.4	72.5
<i>V. Potatoes—very early with presprouting</i>					
1. April . . . . .	7	18	27.0	9.0	33.9
2. May . . . . .	43	49	73.5	24.5	92.1
3. June . . . . .	50	33	49.5	16.5	62.0
Total . . . . .	100	100	150.0	50.0	188.0
<i>VI. Potatoes—early without presprouting</i>					
1. May . . . . .	8	22	33.0	11.0	41.4
2. June . . . . .	33	40	60.0	20.0	75.2
3. July . . . . .	59	38	57.0	19.0	71.4
Total . . . . .	100	100	150.0	50.0	188.0

\* See table 5 for duration.

TABLE 6—*Concluded*

PERIOD*	PER CENT OF HIGHEST AMOUNT		FORMED OR ABSORBED PER MONTH		
	Dry matter	Nutrient	Nitrogen	Phosphoric acid	Potash
<i>VII. Potatoes—medium-early</i>					
			<i>kgm./ha.</i>	<i>kgm./ha.</i>	<i>kgm./ha.</i>
1. May .....	5	14	25.2	8.4	31.5
2. June .....	18	31	55.8	18.6	69.7
3. July .....	59	45	81.0	27.0	101.3
4. August. ....	18	10	18.0	6.0	22.5
Total .....	100	100	180.0	60.0	225.0

*VIII. Potatoes—medium-late*

			<i>kgm./ha.</i>	<i>kgm./ha.</i>	<i>kgm./ha.</i>
1. May . . . . .	3	7	13.9	4.6	17.4
2. June . . . . .	11	23	45.5	15.2	57.0
3. July . . . . .	39	40	79.2	26.4	99.2
4. August . . . . .	44	28	55.4	18.5	69.4
5. September . . . . .	3	2	4.0	1.3	5.0
Total.....	100	100	198.0	66.0	248.0

needs. Neither of these nutrients has a forcing action, and through absorption in the soil both are largely protected against leaching and the formation of solutions of such concentration as to be physiologically injurious. Excessive early nourishment with nitrogen has a more noticeable influence. Apart from the fact that the portion of this nutrient that is not quickly absorbed may easily be lost, the young plants with excess nitrogen are likely to make a rapid and tender growth accompanied by decreased resistance to drought, frost, lodging, and parasites.

Even more undesirable are the results of a delayed supply of plant nutrients. Special pot experiments, partial results of which are given in table 7, indicate that delayed application is much less detrimental to the absorption of nutrients than to the effect on yield. Absorbed nutrients that are not transposed into yield are lost for all practical purposes if, from the increased content, there is no compensatory improvement in quality. This really is a factor only in the case of nitrogen. Secondary growth also is a factor arising out of the absorption of a belatedly supplied nutriment. This growth does not reach maturity and, at least in the case of plants utilized at maturity, is practically valueless or even deleterious because of interference with harvesting. The formation of late shoots is essentially a biological expedient for the purpose of prolonging the ability of the plant to react to the improved growing conditions occurring in the later period of growth. The relative absorption of a delayed



TABLE 7  
*Pot experiments with oats*

TIME OF APPLICATION	EARLY	MEDIUM- EARLY	LATE	DIVIDED
First application . . . . .	At seeding	At emergence	At beginning of stalk growth	At seeding
Second application . . . . .	At beginning of stalk growth	At beginning of stalk growth	At beginning of blossoming	At heading time
<b>I. Nitrogen</b>				
1. Dry matter, in gm. produced by 1 gm. nitrogen fertilizer				
Grain . . . . .	42	39	12	36
Straw and roots . . . . .	77	64	47	66
2. Per cent of nitrogen in dry matter				
Grain . . . . .	1.41	1.57	2.10	1.54
Straw . . . . .	0.38	0.35	0.66	0.37
3. Per cent of nitrogen utilized . . . . .	94	91	87	90
4. Stalks per plant at maturity				
Mature . . . . .	2.5	2.0	1.2	2.0
Immature . . . . .	0	0	1.1	0
<b>II. Phosphoric acid</b>				
1. Dry matter, in gm. produced by 1 gm. phosphoric acid fertilizer				
Grain . . . . .	84	82	4	81
Straw and roots . . . . .	119	100	69	105
2. Per cent of phosphoric acid utilized . . . . .	52	62	63	67
3. Stalks per plant at maturity				
Mature . . . . .	3.3	3.5	1.5	3.5
Immature . . . . .	0	0	1.7	0
<b>III. Potash</b>				
1. Dry matter, in gm. produced by 1 gm. potash				
Grain . . . . .	22	23	9	22
Straw and roots . . . . .	39	33	5	31
2. Per cent of potash utilized . . . . .	94	96	90	93
3. Stalks per plant at maturity				
Mature . . . . .	3.1	3.5	3.3	3.5

fertilization by normal and secondary shoots of the same plant is shown, as an example, in the following results of a special plot experiment with oats:

NUTRIENT	PERCENTAGE OF THE RELATEDLY ABSORBED FERTILIZER	
	In normally growing and maturing stalks	In secondary stalks immature at harvesting
Nitrogen . . . . .	58	42
Phosphoric acid . . . . .	61	39

The yield from the late fertilization was affected only to the extent that valueless second growth increased the difficulty of harvesting.

The more favorable the nutrient supply in the early period of development of the plant, the greater is the absorption in advance of needs, within certain limits determined by inherent characteristics of the plants. The statements for nutrients as a whole hold, more or less, also for the individual nutrients present in the plants. That the absorption of these nutrients proceeds at varying rates according to their physiological function is obviously probable and almost certain, as judged from observations on the physiological activation of the substances dormant in the embryo. The numerous reports on the course of nutrient absorption available to the author, however, show only that absorption of the primary nutrients in greater or lesser degree always precedes growth, and that sometimes one, sometimes another, nutrient is in the lead. Nitrogen frequently is in the lead in nutrient absorption, but it can be reduced to second or third place if another material is copiously supplied. The conception that the availability at a particular time definitely influences the relative absorption of the individual nutrients may be considered as correct in the light of present-day knowledge.

Can nutrient absorption during development show also a cessation or retrogradation? In reports of work at hand, zigzag curves for absorption are very common. These are especially frequent toward the end of growth, indicating that the regression is traceable to replacement of leached or decayed plant parts by subsequent regeneration. In spite of this, the regression can not be ascribed entirely to experimental error or to loss or leaching of necrotic plant tissue. Recent observations on cuticular secretion show rather clearly that the living leaves also continually "sweat." Considerable quantities of nutrients thus are washed off by rain and returned to the soil. The periodic variation in the nutrient content of the plant is thus the difference between absorption and return to the soil. A retrogradation of absorption curve indicates a predominance of the latter.

An indirect influence of weather on nutrient absorption is plainly shown by the great influence of weather on the development of plants. The relationships between weather and nutrient absorption, however, certainly are not limited to this. The common assumption that, in dry weather, crops are low in phosphoric acid but high in protein is a tacit admission that drought shifts the relationships among anabolism, nitrogen absorption, and phosphoric acid absorption in favor of nitrogen and at the expense of phosphoric acid. K pper, to whom the author more than 10 years ago assigned the reexamination of this subject as a doctorate problem (1), believed that he had shown that increasing soil moisture, up to a certain optimum, favored an earlier absorption of all nutrients, whereas dryness of soil had an opposite effect and disturbed absorption relationships to the disadvantage of phosphoric acid, at least until the late stages of development. The relationships between weather and nutrient absorption cannot, in any sense, be considered as exhausted by these

findings. The supporting facts available to the author, however, are not sufficient to warrant the drawing of any further conclusions.

That attacks by parasites affect the nutrition of the plant, and thereby can disturb the normal absorption of nutrients, may be considered as proved. The trend of the influence of the attack is so little known that a discussion at present appears useless. It may be considered as certain, however, that a heavy attack of nematodes, *Phytophthora*, and many other diseases so critically impairs nutrient absorption, along with growth, that studies on badly diseased plants give no conception at all of the normal course of absorption.

### *Summary*

How much Liebscher's theory needed correction may be shown by a comparison of the thesis set forth in the section "Liebscher's teachings" with the following facts:

The physiological characteristics of the species, as well as its environment during growth, have an influence on nutrient absorption. It is not possible, therefore, to speak of a strictly characteristic course of nutrient absorption.

Since nutrient absorption, however, is closely related to the broadly characteristic course of development, there are at least indirect relationships between species and nutrient absorption. The course of nutrient absorption is just as typical as is the development of the plant. Modifications in both arise from internal variabilities of varieties and sports within one species of plants, as well as from their environment during growth.

It is characteristic of the relationships between anabolism and nutrient absorption that the absorption of soil nutrients at first markedly precedes synthesis. Later, a gradual equilibration and, after a high point of development is passed, a reversal of the relationship occur. The author has never observed plants which reached the stage of cessation of synthesis before that of cessation of nutrient absorption. Plants having secondary growth, however, may easily deceptively appear to be an exception.

Nutrient absorption and synthesis end some time before the seed is ripe. In many plants this time interval is masked by secondary growth.

The interrelationships within the general field of development, just as much as growth itself, determine nutrient absorption, dependent, of course, also on duration and seasonal conditions.

None of these relationships, however, are rigid, for all of them are subject to ecological vicissitudes. These are manifested in a storing of nutriment above immediate needs by the plants at a time of plentiful supply. This utilization of supply is closely adjusted to the growth of the plant.

An absorption of phosphoric acid and potash in early growth in advance of physiological need is not deleterious, since these nutrients are not stimulating. On account of soil absorption, they are protected against leaching, and furthermore, they cannot cause an increase in the concentration of the soil solution sufficient to be injurious to the plant. Excessive nutriment in early growth can really be dangerous only in a case of nitrogen. The portion of this nutrient that is not quickly absorbed may be lost, and that absorbed above immediate needs may reduce the resistance of the tender, succulent plants to parasites, frost, and drought.

The plant seeks to obtain the greatest possible advantage from the belatedly absorbed nutriment. Storage in senescent organs and rejuvenation of the plant are ways in which this is done. Potatoes, *Betae*, *Brassicae*, and *Dauci*, for example, rejuvenate themselves mainly by turning green again and forming new leaves. With the *Gramineae*, *Papilionaceae*, and *Cruciferae* the rejuvenation takes the form mostly of suckering. The delayed maturity

resulting from the rejuvenation and increased growth arising from a belated fertilization are undesirable characteristics from the viewpoint of farming.

The delayed supplying of nutriment is much more unfavorable to the efficacy of the nutrient than to its absorption. For example, the stalks of the grains can still store nutrients during late growth without increasing in weight. From a practical standpoint, it is naturally undesirable to have an increase in content without an increase in quality.

The portion of the delayed fertilization used in the formation of secondary growth, likewise serves little or no practical end, since this growth tends to be of little value and, under many circumstances, increases the difficulty of harvesting. Supplying the nutriment too late is, therefore, highly inadvisable.

All these statements apply primarily to nitrogen, phosphoric acid, and potash. A similar relationship for magnesium is almost certain and for lime and other soil nutrients, at least probable.

The maturing leaves usually store large amounts of lime. Although this takes place chiefly at the expense of other parts of the plant, the soil lime also occasionally appears to be involved in this supplementary storing. The physiological significance of this phenomenon does not lie within the scope of this paper.

That the height of nutrient absorption by legumes occurs during the final period of growth is not apparent and, still less, proved. In any case, the author has never succeeded in inducing this experimentally. Ununiformly developed plants probably could misleadingly indicate such behavior, and observations made on such material may also have misled Liebscher.

A marked precedence of nutrient absorption during early growth, according to Liebscher, is dependent on a greatly increased supply of nutrients. That certainly would be correct if there were any characteristically defined precedence of the absorption of nutrients at all. The available observations indicate this often enough. If the individual observations are examined further, however, it will be seen that variations within a species are greater than those between the species. It is almost certain that the relationships between available nutrients and other growth factors more than the class of plant determine the degree of precedence of nutrient absorption.

The absorption of the individual nutrients, in fulfilling their physiological functions, also may reach the end point with varying rapidity. The work bearing on this point does not, however, show to what extent this behavior is dependent on nutrient and species. It has been repeatedly shown that the relative availability of the individual nutrients definitely influences their absorption relationships during the entire growth.

Nutrient absorption can also be negative temporarily. This is explained by the differential character of the periodic changes. According to the relationship of the absorbed nutrients and of those returned to the soil from the epidermis and roots of the plant, the net result may be positive or negative, and the total trend, accordingly, progressive or retrogressive.

Investigations on the course of nutrient absorption permit a deeper insight into the problem only when the plants being investigated are of equal development and health; when conditions for easy and certain differentiation of points of development of the plant as fixed bases are introduced into the investigation; when characteristic behavior is not deduced from one case but from a sufficient number of dependable observations. In this respect, previous work leaves much to be desired and therefore cannot be utilized in the development of a basically sound theory for the problem.

## THE EFFICIENT AND PRACTICAL USE OF FERTILIZERS

### *General*

The data on nutrient requirements given in tables 8 to 10 apply to high yields of average content and include the nutrients contained in the roots and

TABLE 8

*Nutrient absorption by calendar periods*  
I. Basic data for absorption calculations

PLANT	YIELD	REMOVAL*, IN KG./HA.			DURATION OF GROWTH IN DAYS (ROUNDED)	DURATION OF NUTRIENT ABSORPTION IN DAYS (INCLUDING WINTER)
		Nitrogen	Phosphoric acid	Potash		
Winter rye . . . . .	36 grains	92	47	103	280	270
Summer barley . . . . .	34 grains	76	39	73	100	90
Very early potatoes . . . . .	250 tubers	150	50	188	90	80
Medium-late potatoes . . . . .	330 tubers	198	66	248	150	140
Sugar beets . . . . .	400 beets	200	70	290	170	160
Winter rape . . . . .	25 grains	194	89	164	310	280
Peas (Viktoria) . . . . .	30 grains	160	50	110	100	90

## II. Absorption data, in kgm/ha.

PLANTS	FALL TO 11-30	WINTER, 12-1 TO 2-28	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER
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## 1. Nitrogen

Winter rye . . . . .	7.4	2.8	21.0	27.7	28.6	3.7	1.8	....	.. .
Summer barley . . . . .	..	..	..	17.5	35.8	21.3	1.5	....	....
Very early potatoes . . . . .	..	..	..	27.0	73.5	49.5	..	....	....
Medium-late potatoes . . . . .	..	..	..	..	13.9	45.5	79.2	55.4	4.0
Sugar beets . . . . .	..	..	..	..	12.0	40.0	78.0	50.0	20.0
Winter rape . . . . .	77.6	9.7	42.7	44.6	19.4	..	..	....	..
Peas (Viktoria) . . . . .	..	..	..	4.8	52.8	92.8	9.6	....	....

## 2. Phosphoric acid

Winter rye . . . . .	3.8	1.4	10.5	14.1	14.5	1.9	0.8	....	....
Summer barley . . . . .	..	..	..	9.1	18.5	11.0	0.8	....	....
Very early potatoes . . . . .	..	..	..	9.0	24.5	16.5	..	....	....
Medium-late potatoes . . . . .	..	..	..	..	4.6	15.2	26.4	18.5	1.3
Sugar beets . . . . .	..	..	..	..	3.5	10.9	21.0	19.6	14.0
Winter rape . . . . .	35.6	4.5	19.6	20.4	8.9	..	..	....	....
Peas (Viktoria) . . . . .	..	..	..	1.8	17.0	25.8	1.4	....	....

## 3. Potash

Winter rye . . . . .	8.2	3.1	22.6	31.0	32.0	4.1	2.0	..	....
Summer barley . . . . .	..	..	..	16.7	34.1	20.3	1.4	....	....
Very early potatoes . . . . .	..	..	..	33.9	92.1	62.0	..	....	....
Medium-late potatoes . . . . .	..	..	..	..	17.4	57.0	99.2	69.4	5.0
Sugar beets . . . . .	..	..	..	..	14.5	49.3	87.0	87.0	52.2
Winter rape . . . . .	65.6	8.2	36.1	37.7	16.4	..	..	....	....
Peas (Viktoria) . . . . .	..	..	..	5.5	40.7	60.5	..	....	....

\* Including roots and crop residue.

crop residues. Attention is directed to the fact that the data represent arithmetic averages and, therefore, are approximations.

The tables give the monthly and daily needs of the plants in various growth and calendar periods. They thus support the suggestions in the latter part of this section, under "Special Considerations for Some Plant Groups." In order to facilitate summarization, the plants are divided into two contrasting

TABLE 9  
*Daily absorption divided on basis of periods of growth\**

PLANT	AVERAGE DAILY ABSORPTION IN GM./HA. DURING GROWTH PERIOD											
	Nitrogen				Phosphoric acid				Potash			
	1	2	3	1-3	1	2	3	1-3	1	2	3	1-3
Small grains:												
I. Winter barley . . . . .	174	1,381	210	318	82	650	100	150	170	1,350	205	311
II. Winter rye . . . . .	198	1,004	184	327	101	509	94	166	222	1,122	206	366
III. Winter wheat . . . . .	194	1,018	204	329	93	487	98	157	188	983	196	317
IV. Summer barley . . . . .	950	1,270	224	792	494	657	115	410	906	1,210	212	755
Potatoes:												
V. Very early with pre-sprouting . . . . .	938	3,125	0	1,648	312	1,042	0	550	1,175	3,917	0	2,066
VI. Early without pre-sprouting . . . . .	852	3,125	0	1,546	284	1,042	0	515	1,068	3,917	0	1,938
VII. Medium-early . . . . .	882	3,293	0	1,463	294	1,097	0	488	1,104	4,115	0	1,829
VIII. Medium-late . . . . .	884	2,856	0	1,294	295	952	0	431	1,107	3,577	0	1,621

\* Description of periods of growth (see table 5 for days in each period).

PERIOD	SMALL GRAINS	POTATOES
1	Emergence to beginning of stalk growth	Emergence to beginning of blossoming
2	Beginning of stalk growth to blossoming	Beginning of blossoming to beginning of yellowing of foliage
3	Blossoming to maturity	Beginning of yellowing of foliage to maturity

groups containing all the related transition types, according to their absorption of nutrients. The members of these groups are characterized as follows:

1. Nutrient absorption extending over a relatively short time with a distinct point of maximum requirement during the period of greatest absorption, occurring at a time when the soil is rather dormant and the roots of the plant are poorly developed.
2. Nutrient absorption extending over a longer period of time with less distinct point of maximum need; the period of greatest absorption occurring at a time of greater activity in the soil and of better root development.

Plants in intermediate positions between the groups occur as a result of the arbitrary and gradually changing development of the criteria presented for the groups.

Plants in group 1 do best on soils already in a fertile state and/or supplied with quickly acting fertilizers. Slowly acting fertilizer materials should be used only when they are applied soon enough so that they already will have

TABLE 10  
*Daily absorption divided by calendar periods\**

PERIOD	AVERAGE DAILY ABSORPTION							
	Winter barley	Winter rye	Winter wheat	Summer barley	Potatoes			
					Very early with pre- sprout- ing	Early without pre- sprout- ing	Medium early	Medium late

*I. Nitrogen*

	gm./ha.	gm./ha.	gm./ha.	gm./ha.	gm./ha.	gm./ha.	gm./ha.	gm./ha.
Emergence to March 31†	228	328	273	.	.	.	.	.
April	1,033	923	815	583	900	.	.	.
May	997	923	1,029	1,155	2,371	1,064	813	448
June	147	123	437	710	1,650	2,000	1,860	1,517
July	.	58	61	48	.	1,839	2,613	2,555
August	.	.	.	.	.	.	.	1,787
September	.	.	.	.	.	.	.	133

*II. Phosphoric acid*

	107	166	132	.	.	.	.	.
Emergence to March 31	107	166	132	.	.	.	.	.
April	487	470	387	303	300	.	.	.
May	471	468	490	597	790	355	274	148
June	70	63	210	367	550	667	620	507
July	.	26	29	26	.	613	871	852
August	.	.	.	.	.	.	194	597
September	.	.	.	.	.	.	.	43

*III. Potash*

	223	367	265	.	.	.	.	.
Emergence to March 31	223	367	265	.	.	.	.	.
April	1,010	1,033	783	583	1,130	.	.	.
May	974	1,032	990	1,155	2,971	1,335	1,016	561
June	143	137	423	710	2,067	2,507	2,323	1,900
July	.	65	58	48	.	2,303	3,268	3,200
August	.	.	.	.	.	.	726	2,239
September	.	.	.	.	.	.	.	167

\* See table 6.

† 90 days for barley, 85 days for rye and wheat, deducted from the total time for winter dormancy.

been assimilated by the soil and be in an available condition at the period of greatest nutrient absorption by plants.

Plants in group 2, on the other hand, can utilize the less readily available soil nutrients and the slowly acting fertilizers. When quickly acting mate-

rials are applied, the applications should be correlated with the course of nutrient absorption.

These statements apply fundamentally to all nutrients. If in the latter part of this section more attention is paid to nitrogen than to phosphoric acid and potash, this is due to their different behavior in the soil. Soil absorption exerts a marked regulating effect on the activity of phosphoric acid and potash. The course of absorption of these nutrients, however, requires attention, to the extent that in exceptional cases one must determine how late fertilization with phosphoric acid and potash is advisable. Ordinarily the supply of these nutrients for the plants must be assured by an appropriate fertilizer application before or at the time of seeding. In view of its general applicability, this postulation is emphasized at this time and is not repeated with each of the plants. In contrast with its effect on phosphoric acid and potash, soil absorption exerts very little regulating effect on the action of nitrogen, with the exception of the nitrogen in some slowly acting organic fertilizers. The time of application and the period of activity are therefore much closer together. For this reason it is advisable to correlate as closely as possible the time of nitrogen fertilization with the distribution of the requirements of the plants being grown.

In order to avoid erroneous conclusions, one should always keep in mind that there is an interval between the application of fertilizers and the initiation of their action. Since the duration of this interval cannot by any means be generalized, we must content ourselves with the broad statement that the interval varying from days to years, is shortened by increased solubility of the fertilizer, retention of solubility after the fertilizer comes in contact with the soil, absorbability by the plant without time-consuming changes in form, high chemical and biological activity in the soil, damp heat, and great assimilative capacity of the fertilized plant.

#### *Special considerations for some plant groups* ✱

For greater clarity, plants with similar courses of nutrient absorption are arranged in groups, and the brief discussion is limited to especially important representative plants in each group. The basic data for the discussions are to be found in tables 8 to 10.

1. *Fall-sown grains* are typical of plants absorbing nutrients in autumn. The amount of absorption at this time is closely related to fall growth and is therefore dependent on the time of emergence and on fall growing conditions. At the most, 10 per cent of the total nutrient removal may be assigned to the period preceding winter. Late seedings coming up during or after winter make up for lost time in early spring. In severe winters, absorption is at a standstill; in mild winters it never completely ceases, but, even then, the cold season makes a well-defined period in development and nutrition. Only the warm spring sun arouses activity again in both. The maximum point in nutrient absorption occurs during the period of rapid stalk growth. There-



after, from the beginning of blossoming a progressive decrease occurs, absorption ceasing altogether some weeks before maturity. Nutrient absorption extends over 270 to 280 days, including the winter months, of which about 120 days normally fall in the period following winter. If differences due to variation in time of seeding are eliminated, winter barley and wheat are similar in nutrient requirements and absorption to rye, selected as representative of this group of plants in table 10. The small variations occurring with normal seeding and harvesting times can be seen in tables 8 and 9.

The course of nutrient absorption by winter grain makes it appear imperative that the nitrogen be so furnished that most of it is readily available to the plant at the rapidly growing period of stalk development and can be entirely consumed by the beginning of blossoming. The nitrogen requirement before winter is so little with early seeding and even much less with late seeding that it can be met by the soil supply or a very moderate fertilizer application. The much greater need during the period of shoot development can be provided, on soils that are not too light, by applications of calcium cyanamid and slowly acting organic nitrogen fertilizers shortly before seeding or by top-dressing shortly before the end of winter. If a rather large top-dressing is necessary to take care of the needs, either ammonia or nitrate nitrogen in several applications should be given, in view of the extended requirement curve in the period following winter.

In potash-phosphate fertilization, an early top-dressing with superphosphate, Thomasmeal, and high-grade potash salts can very well make up for a lack of fall fertilization. Top-dressings with kainit before and after winter not only serve the purpose of combating weeds but also supply potash to the plant. Barnyard and green manures are suitable for winter grains if their activity is insured at the right time and unfavorable influence on growth and soil structure is prevented.

2. With *summer grains*, nutrient absorption usually begins shortly after emergence at the end of April or the beginning of May and then passes through the same phases as winter grain with a markedly shortened duration and a more sharply defined point of maximum requirement. The short lapse of 100 days and high peak requirements characterize the nutrient absorption of summer grains. This is especially true for early maturing varieties; the maximum and end points in absorption are shifted for late varieties to correspond to their longer growth.

Short duration of absorption, rapid increase in requirement, and marked point of maximum requirement of summer grains indicate the necessity of a quickly available supply of nutriment. This must be assured by a fertile soil and by quickly acting fertilizers, used, at the latest, when the soil is being prepared. Top-dressing is only an expedient, since its action even with ready availability and early application is dependent on the occurrence of rain necessary for dissolving it. Barnyard manure, green manure, and all slowly acting fertilizers thus promise results on summer grains only when they are so used

that they have become assimilated into the soil, at the latest, by the beginning of tillering.

3. *Winter rape* is unusual in that it has two periods of high requirements, shortly before and after the winter season. These peak requirements, combined with the general high level of nutrient needs of this crop, indicate the necessity of a soil in good fertile condition or a fertilization with such materials as will be in an available condition for the plant, at the latest, at the time of the peak requirement preceding winter. For these reasons, manure, correctly applied at the right time, is excellent for rape. An application of calcium cyanamid before seeding supplements very well the nitrogen in the manure. Whether another top-dressing in late winter is necessary to take care of the peak requirement after the winter season depends entirely on the fertility condition of the soil and fall fertilization. When these are not sufficient to fill the needs, a top-dressing with ammonia or nitrate nitrogen is necessary immediately following winter. Naturally, the large amounts of nitrogen necessary for rape will be efficiently utilized by the crop only if a sufficient supply of phosphoric acid and potash is provided.

*Winter rapeseed* is comparable to winter rape in its course of nutrient absorption, but the nutrient needs of the rapeseed are 20 to 30 per cent less than those of the rape, corresponding to the lower levels of yield, and the requirements of the more quickly developing plants must be supplied within a shorter period of time and closer to the cold season of the year. These two later factors make it more difficult to provide the requirements and necessitate a quickly available supply of nutrients.

4. The *hoed crops*<sup>3</sup> are represented in table 8 by medium-late potatoes and sugar beets. They all have a high nutrient requirement, a principal period of absorption rather uniformly spread over the three summer months, a remarkable rise to a maximum requirement in the middle of summer, and a relatively extended absorption curve. Absorption by potatoes of normal maturity ceases the last of August or the first of September, and by sugar beets about a month later, lasting thus 120 and 150 days respectively. The normal cessation of absorption is disturbed commonly by *Phytophthora* attacks on potatoes and not uncommonly by drought and various leaf diseases on sugar beets.

The field varieties of beets, rutabagas, and carrots, as well as the late varieties of the cultivated garden brassicaceous plants (*Brassica oleracea varietas acephala*, *capitata*, *bullata*, *gemmifera*, *botrytis*, and *gongylodes*), are similar to sugar beets and late potatoes except that amount, principal period, and end of nutrient absorption may be shifted materially toward the winter.

It is very significant in the fertilization of all these plants that in addition to their great nutrient needs, the plants require the nutrients at about the

<sup>3</sup> The classification "Hackfrüchte" (literally, hoed crops) is used in Germany to include the brassicaceous along with the tuber and root crops.

same time that these become available in the soil from properly applied barnyard and green manures. Such manures must ordinarily be the basis of the fertilization of the hoed crops. Slow but continuously acting fertilizers serve as good substitutes and supplements of barnyard manure. It is difficult to dispense with the further use of commercial fertilizers, especially to take care of the great peak requirements of the hoed crops. The peak requirements of late potatoes, for instance, are best supplied by an ample application of a properly formulated fertilizer at planting time. Top-dressing with quickly acting commercial fertilizers, in addition to appropriate fertilization at or before planting, is especially suitable for beets and the cabbages, in view of their particular peak needs. That early potatoes and early cabbage must be fertilized quite differently from the late crops will be evident immediately upon examination of tables 8, 9, and 10. Winter cabbage and all other hoed crops with the principal nutrient requirement period coming toward winter are much more dependent on available fertility in the soil and on rapidly acting fertilizers than are the varieties grown in summer.

5. As representative of the *legumes grown for their seed*, the Viktoria pea, very popular in Germany for the production of mature edible peas, is given in table 8. The duration and the time of growth of its early varieties are similar to those of summer barley; its late varieties, to those of oats and spring wheat. The peas, however, are slower in their early development, which shifts nutrient absorption into the summer months. The nitrogen-fixing ability of peas is particularly advantageous in covering the great nitrogen requirements, especially since these are unusually large in June. It is the principal aim of legume fertilization to effect by suitable means a high development of this ability during the longest possible period of growth. A copious supply of potash and phosphate and appropriate liming also indirectly promote nitrogen fixation.

Great variations, however, occur in the growth and nutrient absorption of the legumes, if they actively exercise their tendency to the formation of secondary shoots. This can result in a completely new vegetative growth of the normally maturing plant by the rejuvenated shoots, with a corresponding disarrangement in nutrient absorption. Observations on such plants have given rise to reports that anabolism precedes nutrient absorption in legumes.

The other seed legumes exhibit a fundamentally similar behavior to that of peas in nutrient absorption. Considerable deviation in the amount of nutrients needed and seasonal variation in growth occur, however, which, for lack of space, cannot be gone into here.

6. For *perennial grasses and clovers, hops, asparagus, rhubarb, and other plants with overwintering root stocks*, the following behavior is typical:

During the rootstock formation, which may stretch over several years, a considerable part of the nutrients is utilized by the rootstocks.

During the following years the reserves of assimilated substances and nutriment in the rootstock are drawn upon in spring for the formation of aerial shoots. These reserves are replenished in fall.

The process of alternate spring impoverishment and fall replenishment of the rootstocks of perennial plants is repeated until their death.

Since a well-developed and replenished rootstock is very important for a firm footing and for the whole later development of the perennial plant, the fertilization, above all, must aim at a good rootstock formation and replenishment. The assimilating aerial organs furnish the means for this. Everything that promotes the healthy and vigorous development of these organs is beneficial to the rootstock and thereby to the following year's crop. The crop must therefore be provided for in the preceding summer. Among the means of accomplishing this is the ample supply of nutriment before and during summer. Within a suitable nutrient ratio the form in which the nutrients are supplied is of less importance than the sufficiency of the quantity. It is to be noted in passing that, in addition, the replenishment of the rootstocks should not be impaired by too late cutting of perennial forage crops or by too long a spring harvesting period of asparagus, rhubarb, and similar vegetables.

7. *Head lettuce, endive, spinach, spurry, white mustard, and a series of similar short-lived table and forage crops* have a duration of nutrient absorption corresponding to the short time of development. In addition, growing and harvesting of these crops may be shifted to various seasons, and the harvesting can or must be done long before maturity of seed. The rapid development and short duration of nutrient absorption require readily available fertility in the soil or quickly acting fertilizers. This is more than ever the case when, on account of early or late growing, the nutrient absorption of these plants takes place near the winter months, a time unfavorable for accumulation of nutrients.

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# AN EVALUATION OF THE NEUBAUER AND THE CUNNINGHAM-ELLA AND ASPERGILLUS NIGER METHODS FOR THE DETERMINATION OF THE FERTILIZER NEEDS OF A SOIL

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The Neubauer method for the determination of the fertilizer needs of a soil consists, essentially, of growing rye seedlings and determining their up-take of phosphoric acid and potash at the end of 17 days (3). The Cunninghamella and *Aspergillus niger* methods (2, 3) are recent improvements of the biological (Fungus) methods as developed at the Wisconsin Agricultural Experiment Station. The value and the possibilities of short methods present a serious question to agronomists. The present article is an attempt to give a practical analysis of data obtained by the Neubauer and by the Fungus methods. Reference is also made to the results from a rapid chemical test method as followed at the Indiana Station.<sup>1</sup>

## DESCRIPTION OF SOILS USED

One hundred twenty-nine samples of soil, representing 9 distinct soil types, 1 soil type phase, and 1 land type, were used in the study. The soil types and phase, with special regard to their supplies of phosphoric acid and potash, are described briefly as follows:

*Memphis silt loam*, from the outset of the field plot experiments in 1909, proved to be extra well supplied with both phosphoric acid and potash. Of recent years, mild response has been noted to applications of both elements for each of a number of crops, including barley and cotton, but not definitely for corn, which, in the series on range 4 has been grown continuously in fertilizer experiments on the same plots for 26 years. During this period the entire crop, including both ear corn and stover, was removed annually. Check plot 21, receiving no fertilizer, gave an average yield for the 5 years 1931-1935 of 14.5 bushels of corn and 0.68 ton of stover per acre. Plot 22, receiving 200 pounds of superphosphate and 50 pounds of muriate of potash per acre annually, gave an average yield of 17.3 bushels of corn and 0.80 ton of stover per

<sup>1</sup> The Neubauer tests were made by B. W. Hatcher and J. S. Dempster under the supervision of Dr. S. F. Thornton, of the Indiana Agricultural Experiment Station (Purdue). The biological tests were made by Dr. Adolf Mehlich, of the Wisconsin Agricultural Experiment Station. All tests were carried out at the Tennessee Agricultural Experiment Station at Knoxville. The project was cooperative between the Tennessee Valley Authority and the Wisconsin and Tennessee Stations.

acre. Plot 23, receiving the same amounts of phosphate and potash as plot 29 and an annual application of 100 pounds of nitrate of soda in addition, gave an average yield of 28.9 bushels of corn and 1.29 tons of stover per acre. Plot 24, which received only the nitrate application of 100 pounds per acre, yielded an average of 32.1 bushels of corn per acre and 1.20 tons of stover per acre. On range 2, unfertilized plots produced in the last 3 of the 26 years of continuous cropping in a 3-year rotation, annual yields of nearly 2 tons of cow-pea hay, 1,500 pounds of seed cotton, and 50 bushels of corn per acre.

*Memphis silt loam, white-land phase*, has an appreciably greater need of potash than has typical Memphis silt loam. The yield of cotton is greatly increased by the application of 50 pounds per acre of muriate of potash, which appears to meet the requirement. The yield of the clover and grass crop is increased to a less extent by a potash application; and that of corn and oats, none at all. In recent years phosphoric acid has appeared of value. This soil phase is undoubtedly of a lower order of fertility than typical Memphis silt loam.

*Huntington loam* is of alluvial origin and forms what is commonly known as second-bench land on Tennessee River. It is, perhaps, the best type of soil in East Tennessee and is more drouth-resistant than the uplands. The supplies of both phosphoric acid and potash are so good that even after 30 years of cropping in the experimental rotation the unmanured and unfertilized plot 1, range A, produced nearly 3 tons of cured hay per acre in 1933 and over 70 bushels of corn per acre in 1934.

*Cumberland loam* is a naturally fertile soil. Prior to the beginning of the field experiments in 1905, it had been in grass for many years but had suffered little loss of plant nutrients from either mowing or pasturing. During the experimental period, double cropping—cowpeas in summer and wheat in winter—has been practiced on all plots except the 7's. The cowpea crops were turned under annually on all plots except G4, G5, I4, F6, G6, and G8, where they were removed as hay. Yields for the first 20 years are reported in Bulletin 135 of the Tennessee Station. The response to phosphate was mild from the outset and has been obscured for some years by the much greater need of potash. The response to potash gradually became evident with marked deficiency in recent years of all plots not receiving potash, those where the cowpea crop was turned under annually and only the wheat crop removed, as well as those where both cowpea and wheat crops were removed.

*Fullerton silt loam*, an important upland type in East Tennessee, is well known to be very poor in phosphoric acid and only moderately supplied with potash. Corn in few places responds to an application of potash. On the other hand, in many places, annual legumes, such as cowpeas and soybeans for hay; truck crops; and tobacco are responsive to potash.

*Decatur silt loam* is naturally much more fertile than the Fullerton. In fact, Decatur uplands are rated the best in East Tennessee. Response to

phosphoric acid, however, is general. The potash supply is usually good; consequently, under livestock farming, with the careful saving and use of farmyard manure, it need not be considered. Under usual conditions, potash is not recommended for either corn or wheat but may be used to advantage for truck crops and tobacco.

*Hartsells fine sandy loam* is a very poor type of soil found on the Cumberland Plateau. The need of phosphate is especially pronounced. The potash supply is relatively good as far as corn, oats, and wheat are concerned, but a potash fertilizer can be used profitably in many places for hay crops and usually for potatoes.

*Mericourt silt loam* is named for the substation at which the samples were taken. This soil is naturally very poor in phosphoric acid and is not well supplied with potash. In general behavior it resembles Fullerton silt loam.

*Montevallo silt loam* is a poor type of soil derived from shale. It is especially responsive to phosphoric acid, but the supply of potash is usually rated as fair to good, or appreciably better than that of Fullerton silt loam.

*Colbert silt loam*, derived from clay limestone, is rather variable in natural fertility. According to the results of fertilizer experiments, the greatest need is for phosphoric acid, and little response to potash has been shown by any of the common farm crops.

## SUMMARY OF RELATIVE STANDING OF SOILS ON BASIS OF FIELD EXPERIMENTS

### PHOSPHORIC ACID

According to the results of field experiments, Memphis silt loam, including the white-land phase, and Huntington loam have the best natural supply of phosphoric acid. Where they have received annual applications of 200 pounds per acre of 16 per cent superphosphate over a long period, as in the experimental series where the samples were obtained, the phosphorus content of any of them would be expected to be high.

Cumberland loam ranks a little below the Memphis and the Huntington soils, but where phosphated, as it has been annually for 30 years in the experimental series from which the samples were taken, the immediate supply of available phosphoric acid is considered to be good. The annual rate of application per acre for the period 1905-1926 was 200 pounds of 16 per cent superphosphate or its equivalent. Thereafter the annual application was 150 pounds.

Of the remaining soil types, the Decatur ranks first in supply of this element but below Cumberland loam.

The Fullerton, Hartsells, Mericourt, and Montevallo soils are rated the poorest of all in phosphoric acid.

It should be noted that only unfertilized soil samples from check plots in field experiments were used for the Fullerton, Decatur, Montevallo, and Col-



bert soils. Both phosphated and unphosphated plots are represented in all the others, except soil 86, which is a sandy but highly productive alluvial soil that, so far as is known, had never received fertilizer of any kind.

#### POTASH

From the results of both field experiments and farmers' experience, Huntington loam and the sandy river soil, No. 86, would be expected to be, perhaps, the best supplied with potash of all the soils used. Exclusive of the white-land phase, Memphis silt loam would rank next best; the Cumberland, third; the Decatur, fourth; and the Montevallo, Colbert, Hartsells, Mericourt, and Fullerton soils and the white-land phase of Memphis silt loam in order as listed, but with little choice among the last three.

In the experimental series the usual application was 50 pounds of muriate of potash per acre annually. This was the rate of application on Cumberland loam during the period 1905-1926; thereafter, 75 pounds per acre was applied annually.

#### SOIL SAMPLES

All soil samples were taken in the fall of 1935. The depth of sampling was 6-8 inches, depending either on the depth of plowing or on the distance to the well-defined subsoil. Each plot was 1/40 acre, as a rule. Many plots had records of fertilizer treatments and crop yields for 25 or more years. Special care was taken to obtain representative samples. Ten subsoil samples were taken, to a uniform depth, from each plot or half plot, as in the case of both Cumberland loam and Memphis silt loam. They were well mixed, and a laboratory sample of about 3 quarts was prepared. The samples used in each method of testing were considered to be virtually identical.

#### GENERAL STATEMENT OF PROBLEM

One of the important problems is to determine as far as possible the comparative merits of the methods. Unfortunately, there is no way of setting up positive standards for any soil; that is, there is no method by which the actual number of pounds per acre of immediately available phosphoric acid or potash can be determined. For this reason, no attempt was made in the soil description to give more than the general situation for each soil. Fortunately, it appears possible to reach certain conclusions based on a careful survey of all the evidence at hand, the known soil treatments, the field-crop data, and the indications as to liability to error inherent in a method.

It is, of course, important to understand that the essential requirement of either method is the getting of dependable comparative data from which practical conclusions as to fertilizer needs may be reached. Hence, the fact that the general level of the findings by one of the methods is higher than that by the other, is of minor interest.

The data calculated to pounds per acre as found by each method are given in table 1.

TABLE 1

*Available plant nutrients in various soils as determined by both the Neubauer and the Fungus methods*

(Data calculated to pounds per acre—2,000,000 pounds soil)

SOIL NUM- BER	SOURCE OF SOIL	KIND OF SOIL	RANGE AND PLOT	PREVIOUS TREATMENT	METHOD AND FINDINGS			
					Neubauer		Fungus	
					P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
6	W. T. Station	Memphis silt loam, white- land phase	A 1	None	42	60	44	166
7			4	PK	90	108	74	188
8			5	P	64	134	86	148
9			6	K	56	230	44	236
10			B 1	PK	64	158	52	250
11			2	P	90	194	98	216
12			3	PK	86	218	58	296
13	W. T. Station	Memphis silt loam	2 13	None	76	242	64	292
14			14	PK	122	242	104	340
15			15	P	110	194	98	296
16			18	None	78	182	64	264
17			19	PK	120	326	104	324
18			20	P	146	218	92	330
19			3 1	K	40	108	44	250
20			2	P	54	108	64	188
21			3	PK	54	218	58	194
22			10	K	66	60	64	220
23			11	P	130	96	110	172
24			12	PK	102	96	118	166
25			19	K	32	134	52	250
26			20	P	70	72	70	194
27			21	PK	62	134	80	216
28			4 21	None	54	194	98	256
29			22	PK	90	302	144	328
30			23	PK	78	242	144	308
31			24	O	40	182	80	220
32			25	O	64	302	104	292
33			26	PK	132	484	110	382
34			27	PK	112	424	132	404
82	Knoxville Station	Huntington loam	A 1	None	22	108	84	160
83			2	Manure, PK	42	158	194	210
84			3	Manure, PK	62	182	152	226
85			8	Manure	70	412	152	372
86	Knoxville Station	River soil		None	2	254	44	330
87	Knoxville Station	Cumberland loam	F 4	P	28	158	158	128
88			4L	P	46	96	118	148
89			5	PK	48	134	132	256
90			5L	PK	24	158	138	256
91			6	Manure	42	134	124	246
92			6L	Manure	42	108	138	236

TABLE 1—Continued

SOIL NUM- BER	SOURCE OF SOIL	KIND OF SOIL	RANGE AND PLOT	PREVIOUS TREATMENT	METHOD AND FINDINGS			
					Neubauer		Fungus	
					P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
93	Knoxville Station	Cumberland loam	7	P	46	230	132	312
94			8	PK	68	134	132	260
95			8L	PK	60	108	118	256
96			G 4	P	52	36	118	110
97			4L	P	46	108	124	128
98			5	PK	52	170	118	182
99			5L	PK	36	122	98	194
100			6	Manure, PK	52	266	104	296
101			6L	Manure, PK	28	194	118	246
102			7	P	50	218	118	274
103			8	PK	56	60	104	200
104			8L	PK	34	96	98	182
105			H 4	None	18	60	74	120
106			4L	None	26	122	74	116
107			5	PK	60	254	138	260
108			5L	PK	60	290	118	308
109			6	PK	32	194	92	288
110			6L	PK	16	206	86	270
111			7		50	376	132	336
112			8	PK	46	212	138	376
113			8L	PK	64	472	138	408
114			I 4	None	22	146	74	120
115			4L	None	18	134	64	110
116			5	PK	46	312	98	292
117			5L	PK	40	242	110	270
118			6	PK	32	254	92	274
119			6L	PK	28	206	74	256
120			7	None	20	170	98	240
121			8	PK	64	302	104	330
122			8L	PK	38	326	110	380
123			J 4	PK	32	206	124	264
124			4L	PK	38	278	158	300
125			5	PK	72	266	132	250
126			5L	PK	48	194	144	240
127			6	PK	32	254	92	292
128			6L	PK	20	134	98	256
129			7	None	44	242	98	328
130			8	K	28	194	86	288
131			8L	K	8	230	92	278
4	Jefferson Co.	Fullerton silt loam		None	34	60	52	104
143	Ed Walker		Corn	None	0	122	38	204
144	C. C. Troutman		Corn	None	0	96	30	148
145	E. G. Acuff		Corn	None	0	182	34	296
146	J. E. Wilson		Corn	None	0	122	34	200
149	James Walker		Corn	None	10	134	38	250
150	Poor Farm		Corn	None	0	72	48	128

TABLE 1—*Concluded*

SOIL NUMBER	SOURCE OF SOIL	KIND OF SOIL	RANGE AND PLOT	PREVIOUS TREATMENT	METHOD AND FINDINGS			
					Neubauer		Fungus	
					P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
151	J. M. D. Nelson	Fullerton silt loam	Corn	None	0	108	48	188
152	J. T. Hodge		Corn	None	0	72	44	110
153	Roy French		Wheat	None	0	194	34	292
155	J. C. Wilson		Wheat	None	0	158	24	232
156	E. G. Acuff		Wheat	None	12	194	38	236
158	Ed Walker		Wheat	None	6	60	34	188
159	J. M. D. Nelson		Potato	None	8	146	64	236
160	J. C. Wilson		Potato	None	20	108	74	250
168	J. C. Wilson		Crimson clover	None	18	134	58	200
169	A. W. Kirby		Barley	None	0	122	64	182
171	Knox Co.		Rims	None	28	134	38	160
2	Jefferson Co.	Decatur silt loam			42	194	64	282
154	S. E. Ray		Wheat	None	8	146	74	240
161	H. L. Howard		Potato	None	8	108	34	200
163	Cotton Farm		Soybean	None	18	254	64	328
165	Gentry		Flax	None	26	72	86	140
166	Gentry		Flax	None	16	60	98	166
1	Cumberland Co.	Hartsells fine sandy loam		None	32	158	34	264
132	Jas. Smith		A 1 4	PK	8	24	44	166
133			A 2 4	PK	8	72	34	194
134			A 3 4	PK	2	96	64	204
135			A 4 4	O	4	146	24	260
136			A 5 4	PK	16	84	86	194
137			A 3 5	P	10	84	74	148
138			A 4 5	O	10	146	44	240
139			A 5 5	P	26	158	110	220
140				None	0	170	80	324
141				None	0	194	34	300
142	Homestead			None	10	170	24	260
65	Mericourt Station	Mericourt silt loam	3 9S	PK	36	170	118	304
66			3 20S	P	16	146	98	172
67			0 9	O	0	314	48	328
68			3 9N	PK	34	182	86	270
69			3 20N	P	16	96	70	198
70			0 8	P	10	122	58	348
3	Jefferson Co.	Montevallo silt loam		None	40	374	58	428
148	F. N. Hamilton		Corn	None	2	182	34	236
162	Cotton Farm		Soybean	None	16	158	44	250
167	D. H. Tunnell		Corn	None	0	108	74	98
172	Montvale		Wheat		16	48	58	120
5	Russell Ford	Colbert silt loam		None	24	72	74	120
147	J. D. Shipe		Corn	None	0	108	38	216
157	J. D. Shipe		Wheat	None	6	36	30	98

## DISCUSSION OF DATA

## COMPARATIVE ADAPTABILITY OF THE NEUBAUER AND FUNGUS METHODS TO DIFFERENT SOIL TYPES

*Phosphoric acid*

The data of table 1 show conclusively that both the Neubauer and the Cunninghamella methods make positive distinctions between phosphated and unphosphated plots in an experimental series, as well as between certain of the soil types with regard to the supply of available phosphoric acid. It is noticeable that for the river soil and for 8 of the soil types, beginning with Huntington loam and ending with Colbert silt loam, the results were on a consistently higher level by the Cunninghamella method than by the Neubauer method. On the other hand, for Memphis silt loam and its white-land phase, involving a total of 29 soil samples, the data from the Cunninghamella method were at nearly the same level as those from the Neubauer method. This inconsistency is so outstanding as to require consideration, for it is evident that one or the other of the methods must be at fault. Field experiments, carried out for 26 years on these soils, showed the soils to be exceptionally well supplied with phosphoric acid. The Cunninghamella method, therefore, though showing differences due to soil treatment, gives results on decidedly too low a level for Memphis silt loam.

Although Memphis silt loam affords an outstanding example of disagreement, as far as the comparative placement of soil types is concerned, further consideration of the data raises a similar question with regard to other soils. Cumberland loam, for example, is a fertile soil, producing much larger crops than do most types and appreciably less responsive to phosphate treatment. This rating is indicated clearly by the Cunninghamella method. On the other hand, the results by the Neubauer method are decidedly too low.

In the sandy river soil, No. 86, a very low content of  $P_2O_5$ , as found by both methods, is probably correct, but the practical interpretation of the result would have to be made on an entirely different basis from that adapted to an upland soil; the river soil was not found responsive to  $P_2O_5$ , probably on account of the favorable permeability conditions. The conclusion is therefore reached that different soil types may require different standards of interpretation by either method.

Attention is directed to another matter, that is, the frequency with which the Neubauer method gives a zero content of phosphoric acid for soils low in this element. These soils are indicated as very deficient, it is true, but they always contain a positive supply of available phosphoric acid, most of them having produced, without phosphate, approximately 25 bushels of corn per acre the year the soil samples were taken. The matter of zero results raises the question of liability to error, which may account for some rather wide discrepancies between results obtained by the two methods for individual soil samples.

*Potash*

The potash data by the two methods appear, in a general way, to be more consistent, so far as all soil types are concerned, than the data for phosphoric acid; that is, there is no pronounced change in the level for any particular soil type. The effects of fertilizer applications are, in general, plainly indicated by each method, but the individual disagreements are even more numerous than in the case of  $P_2O_5$ .

TABLE 2

*Tentative standards\* for comparison of data obtained by the Neubauer and Fungus methods*  
(In pounds per acre)

	VERY LOW	LOW	MEDIUM	HIGH	VERY HIGH
Neubauer method:					
$P_2O_5$ . . . . .	1-20	21-40	41-60	61-80	>80
$K_2O$ . . . . .	1-100	101-150	151-200	201-250	>250
Fungus methods:					
$P_2O_5$ . . . . .	1-50	51-90	91-130	131-170	>170
$K_2O$ . . . . .	1-150	151-220	221-290	291-360	>360

\* The general import of the terms used is as follows:

$P_2O_5$ :

Very low, extremely deficient in  $P_2O_5$ .

Low, deficient in  $P_2O_5$  for all crops. Use of phosphate an essential to profitable farming.

Medium, response to  $P_2O_5$  moderate to none. No special need for  $P_2O_5$  under good livestock system of farming. Cotton, tobacco, and truck crops usually show response.

High, no immediate response to  $P_2O_5$  by any crop.

Very high, will stand more than a year's cropping without response to  $P_2O_5$ .

$K_2O$ :

Very low, nearly all crops benefited, except possibly corn and oats, both of which would likely respond to  $K_2O$  after removal of a succession of hay crops such as lespedeza.

Low, hay, truck crops, tobacco, and cotton respond markedly to applications of  $K_2O$ . Not usually needed by corn and oats.

Medium,  $K_2O$  not required in livestock farming under good methods. Under many conditions, moderate applications of  $K_2O$  are profitable for truck crops and tobacco. Little response by general farm crops.

High, no immediate response to  $K_2O$  by any crop.

Very high, will stand more than a year's crop removal without response to potash.

## STANDARDS OF INTERPRETATION

In the pursuit of the present study it appeared desirable to set up standards for the comparative study of the data. These standards may not be those finally adopted for the purpose of making practical recommendations for Tennessee soils, but they are considered to be approximately in accord with the results of the field experiments. Standards for the Neubauer method were delimited in groups somewhat arbitrarily, but with regard to the field data. Standards were then developed for the Fungus methods with a view to making

the two sets comparable, if possible. To accomplish this result, dependence was placed only on cut-and-dry procedure. The standards, as obtained in this way, are shown in table 2.

TABLE 3

Group placements of available  $P_2O_5$  for each of 10 soils as indicated by both the Neubauer and the Cunninghamella methods

GROUP	MEMPHIS SILT LOAM		WHITE- LAND PHASE MEMPHIS SILT LOAM		HUNT- INGTON LOAM		CUMBER- LAND LOAM		FULLER- TON SILT LOAM		DECA- TUR SILT LOAM		HART- SELLS FINE SANDY LOAM		MERI- COURT SILT LOAM		MONTE- VALLO SILT LOAM		COL- BERT SILT LOAM	
	N.*	C.†	N.	C.	N.	C.	N.	C.	N.	C.	N.	C.	N.	C.	N.	C.	N.	C.	N.	C.
Very low...	0	1	0	2			6	0	16	13	4	1	10	7	4	1	4	2	2	2
Low...	3	9	0	4	1	1	16	7	2	5	1	5	2	4	2	3	1	3	1	1
Medium...	3	9	2	1	1	0	19	25	0	0	1	0	0	1	0	2	0	0	0	0
High...	7	3	2	0	2	2	4	13	0	0	0	0	0	0	0	0	0	0	0	0
Very high.	9	0	3	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total num- ber sam- ples...	22	22	7	7	4	4	45	45	18	18	6	6	12	12	6	6	5	5	3	3

\* N. = Neubauer.

† C. = Cunninghamella.

TABLE 4

Group placements of available  $K_2O$  for each of 10 soils as indicated by both the Neubauer and the Aspergillus niger methods

GROUP	MEMPHIS SILT LOAM		WHITE- LAND PHASE MEMPHIS SILT LOAM		HUNT- INGTON LOAM		CUMBER- LAND LOAM		FULLER- TON SILT LOAM		DECA- TUR SILT LOAM		HART- SELLS FINE SANDY LOAM		MERI- COURT SILT FOAM		MONTE- VALLO SILT LOAM		COL- BERT SILT LOAM	
	N.*	A.N.†	N.	A.N.	N.	A.N.	N.	A.N.	N.	A.N.	N.	A.N.	N.	A.N.	N.	A.N.	N.	A.N.	N.	A.N.
Very low...	4	0	1	1	1	0	5	8	5	4	2	1	6	1	1	0	1	2	2	2
Low...	4	8	2	3	1	2	11	4	9	7	2	2	1	5	2	2	1	0	1	1
Medium...	4	4	2	2	1	1	8	21	4	5	1	2	5	4	2	1	2	2	0	0
High...	5	8	2	1	2	1	9	8	0	2	1	1	0	2	0	3	0	0	0	0
Very high.	5	2	0	0	0	1	12	4	0	0	0	0	0	0	1	0	1	1	0	0
Total num- ber sam- ples.....	22	22	7	7	5	5	45	45	18	18	6	6	12	12	6	6	5	5	3	3

\* N. = Neubauer.

† A.N. = *Aspergillus niger*.

#### COMPARATIVE SOIL RATINGS ON THE BASIS OF GROUP STANDARDS

By the aid of the standards, comparison of the data by the two methods is simplified, as illustrated in tables 3 and 4. These tables emphasize the general conclusions previously reached, both as to the marked similarity of the place-

ments obtained by both methods for the majority of the soils and as to the dissimilar placements in respect to  $P_2O_5$  for both Memphis silt loam and Cumberland loam, the Neubauer method giving high, but apparently proper, indications for the former soil type but decidedly too low indications for the latter soil type. It is important to consider that the data for each type of soil in both tables are general in nature, and that little light is thrown, therefore, on the numerous individual inconsistencies noticeable in table 1, a subject which will now be discussed.

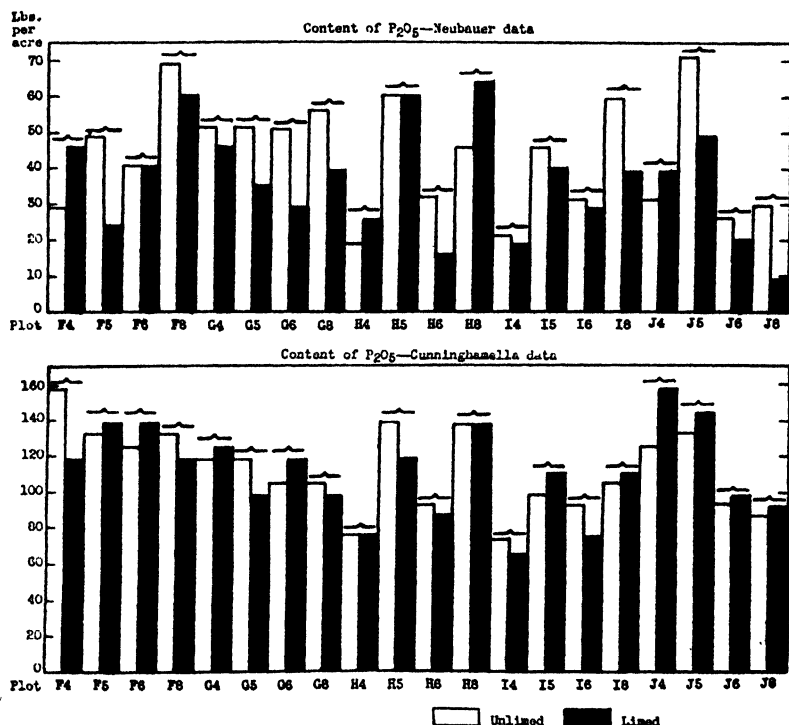


FIG. 1.  $P_2O_5$  CONTENT OF LIMED AND UNLIMED PLOT SECTIONS OF CUMBERLAND LOAM AT THE KNOXVILLE STATION, AS DETERMINED BY THE NEUBAUER AND THE CUNNINGHAMELLA METHODS

#### INHERENT SOURCE OF ERROR

Every analytical method carries certain inherent error; that is, no method is absolutely accurate. Obviously, methods as different as those under consideration might differ in the extent or seriousness of this error. Figures 1 and 2 and table 5 were prepared in order to throw light on this subject. The basic data are found in the Cumberland loam group of table 1, which includes all the plots having limed and unlimed sections. Fortunately, for the present purpose, the sections of any one plot may be considered as duplicates, to the extent that they would be expected to be closely alike in their contents of



$P_2O_5$  and  $K_2O$ . Applications of 1 ton of burnt lime per acre were made twice in the 30-year period, the first time in 1905, and the second in 1917. The effects of liming on crop yield have been noticeable even in recent years, as shown in table 6, which gives the annual crop production and the percentage variation from the plot average between the limed and the unlimed sections.

In order to present the analytical findings on a comparable basis for the Neubauer and the Fungus methods, the percentage difference between the data for the limed and unlimed section of each plot is given in table 5, the

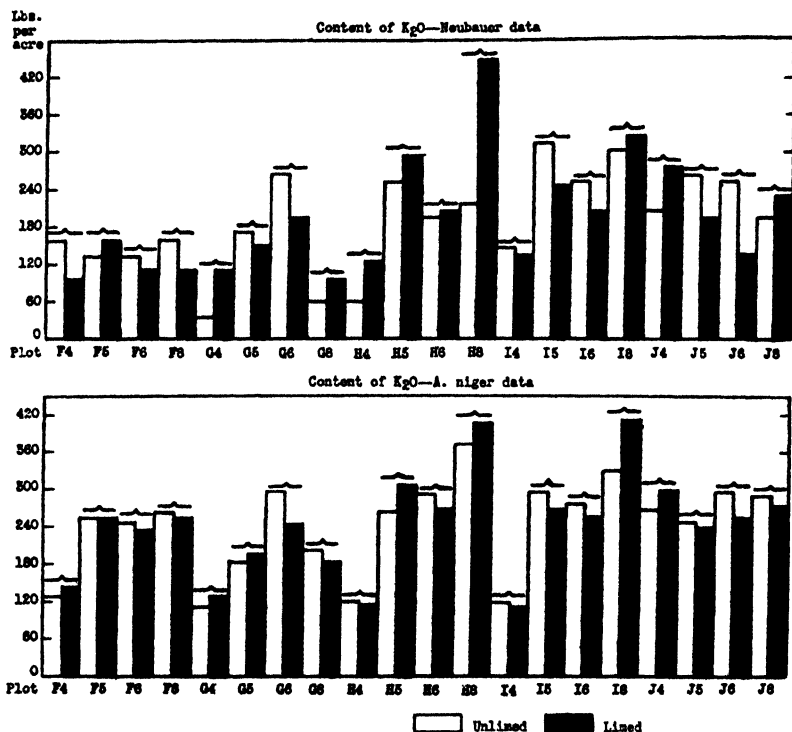


FIG. 2.  $K_2O$  CONTENT OF LIMED AND UNLIMED PLOT SECTIONS OF CUMBERLAND LOAM AT THE KNOXVILLE STATION, AS DETERMINED BY THE NEUBAUER AND THE ASPERGILLUS NIGER METHODS

basis of calculation being the average number of pounds of  $P_2O_5$  or of  $K_2O$  for the two sections of a plot. The maximum difference for  $P_2O_5$  was 111 per cent by the Neubauer method, as compared with 29 per cent by the Cunninghamella method; and 9 plots differed by 40 or more per cent by the former method, whereas only 3 plots differed by more than 20 per cent by the latter method. Similarly, the maximum difference for potash was 100 per cent by the Neubauer method, as compared with only 19 per cent by the *A. niger* method. The average differences for  $P_2O_5$  and  $K_2O$  by the Neubauer method

were 37 and 34 per cent, respectively, against only 11 and 9 per cent by the Fungus methods. There must, of course, be some actual soil differences, but these would be the same for each method. How much of the difference can be attributed to the soil is not known, but it can be reasonably assumed to be, on the average, less than 11 per cent for  $P_2O_5$  and less than 9 per cent for potash, which represent the additive effects of both the soil difference and the

TABLE 5

*Variation in  $P_2O_5$  and  $K_2O$  content between unlimed and limed plot sections—Cumberland loam at the Knoxville Station*

PLOT	NEUBAUER METHOD		FUNGUS METHODS	
	$P_2O_5$	$K_2O$	$P_2O_5$	$K_2O$
	per cent	per cent	per cent	per cent
F-4	49	49	29	15
F-5	67	16	4	0
F-6	0	21	11	4
F-8	13	21	11	2
G-4	12	100	5	15
G-5	36	34	19	6
G-6	60	31	13	19
G-8	49	46	6	9
H-4	36	68	0	3
H-5	0	13	16	17
H-6	66	6	7	6
H-8	33	73	0	8
I-4	20	9	15	9
I-5	14	25	12	8
I-6	13	21	22	7
I-8	51	8	6	15
J-4	17	31	24	13
J-5	40	31	9	4
J-6	46	62	6	13
J-8	111	17	7	4
Average variation.	37	34	11	9

inherent error in the Fungus methods. This estimate is corroborated by the crop data of table 6. Undoubtedly the differences in crop yields between the limed and the unlimed halves of the plots must be attributed chiefly to the effects of the liming. Even so, the total difference amounts to only 11.32 per cent, on the average, when calculated in a manner similar to that by which the percentages were obtained for the soil analytical data given in table 5. The conclusion is reached, therefore, that the Fungus methods far surpass the Neubauer method, insofar as inherent liability to error is concerned. In fact, this liability to error appeared to be a serious handicap to the Neubauer method.

## COMPARATIVE AVAILABILITY OF DIFFERENT PHOSPHATES

Short methods are sometimes recommended as a means of obtaining an index of the availability of different phosphates when applied to the soil. Table 7 gives the comparative rating in availability of eight different phosphates for each of five soils known to be deficient in phosphoric acid, mono-

TABLE 6

*Relative productivity of Cumberland loam plots, as indicated by crop production for 5 years, 1931-1935. Total average annual yields of cowpeas and wheat, both straw and grain included*

(Both cowpeas and wheat grown annually on all plots except on H-5, where only wheat was grown, and on H-8, where only cowpeas were grown)

PLOT	FERTILIZER	DISPOSITION OF COWPEA CROPS	UNLIMED	LIMED	AVERAGE	PERCENTAGE DIFFERENCES IN PRODUCTION BETWEEN UNLIMED AND LIMED HALVES, ON BASIS OF PLOT AVERAGE
			cwt.	cwt.	cwt.	
F-4	P	Turned under	30.9	32.7	32.7	5.50
5	PK	Turned under	51.3	50.8	51.1	0.98
6	Manure	Removed	64.5	65.7	65.1	1.84
8	PK	Turned under	68.1	69.7	68.9	2.32
G-4	P	Removed	23.8	20.2	22.0	16.36
5	PK	Removed	32.9	39.5	36.2	18.23
6	Manure and PK	Removed	58.5	62.4	60.5	6.45
8	PK	Removed	35.8	45.8	40.8	24.51
H-4	None	Turned under	35.2	40.9	38.1	14.96
5	PK	None grown	20.0	22.7	21.4	13.09
6	PK	Turned under	49.7	60.3	55.0	19.27
8	PK	Turned under	30.6	36.2	33.4	16.73
I-4	None	Removed	20.0	24.2	22.2	18.47
5	PK	Turned under	53.5	59.7	56.6	7.42
6	PK	Turned under	51.9	62.0	57.0	17.72
8	PK	Turned under	59.5	66.1	61.8	10.68
J-4	PK	Turned under	54.2	57.1	55.7	5.21
5	PK	Turned under	56.5	62.0	59.3	9.27
6	PK	Turned under	47.7	55.6	51.7	15.28
8	K	Turned under	48.1	59.1	48.6	2.06
Average .....			44.5	49.1	46.9	11.32

calcium phosphate being taken as the standard of comparison, or 100 per cent. Meta-A was much more readily water soluble than was Meta-B. As determined by the Neubauer method, the average standing of the phosphates was monocalcium, first, 100 per cent; fused, second, 97 per cent; dicalcium, third, 92 per cent; triple super, fourth, 74 per cent; meta-A, fifth, 64 per cent;

tricalcium, sixth, 60 per cent; meta-B, seventh, 18 per cent; and rock phosphate, eighth, 13 per cent. As determined by the Cunninghamella method, the order was monocalcium, first, 100 per cent; triple super, second, 96 per cent; dicalcium, third, 87 per cent; fused, fourth, 81 per cent; meta-A, fifth, 70 per cent; tricalcium, sixth, 52 per cent; meta-B, seventh, 43 per cent; and rock phosphate, eighth, 6 per cent.

Comparative field trials with various phosphates were made on all the soils except the Decatur. Corn, wheat, millet, cowpeas, soybeans, and potatoes were the crops used. The trials were not sufficient to establish differences, if any, in the availability of the phosphates as affected by type of soil. No positive difference appeared in effects on crop yield between monocalcium,

TABLE 7

*Comparative availability of different phosphates as determined by the Neubauer and Cunninghamella methods—monocalcium phosphate taken as the standard, or 100 per cent*

PHOSPHATE	COLBERT		DECATUR		FULLERTON		HARTSELLS		MONTEVALLO	
	N.*	C.†	N.	C.	N.	C.	N.	C.	N.	C.
Monocalcium . . . . .	100	100	100	100	100	100	100	100	100	100
Dicalcium . . . . .	97	74	75	106	102	81	82	91	104	84
Fused . . . . .	.	..	85	83	..	..	110	84	97	80
Meta-A . . . . .	41	81	70	100	72	66	68	47	69	54
Meta-B . . . . .	39	54	5	69	9	41	3	25	32	27
Rock phosphate . . . . .			0	9	.	..	0	7	38	3
Tricalcium . . . . .	80	56	28	51	76	43	34	77	84	35
Triple super . . . . .	66	92	68	106	102	87	54	94	81	100

\* N. = Neubauer.

† C. = Cunninghamella.

triple super, dicalcium, and calcium metaphosphate, pound for pound of total  $P_2O_5$  applied; on the other hand, fused and tricalcium phosphate almost always took an appreciably lower ranking, which was not unexpected, in view of the fact that probably not over three fourths of the original fluorine content of the rock had been displaced in the process of manufacture.

As to the results by the methods under comparison, not only is there an evident lack of harmony, but neither method indicated the proper standing of metaphosphate, which was rated much too low. Otherwise, the Cunninghamella results are closely in harmony with the field data. On the other hand, the results by the Neubauer method are decidedly at variance with the field data and with expectations based on composition of the materials. The phosphoric acid in triple superphosphate, for example, is virtually all in the monocalcium form, but by the Neubauer method its rating was only 74 per cent. Another example is the high rating of 97 per cent for fused phosphate, which, as previously stated, was almost always appreciably excelled by the four leading phosphates.

## RAPID CHEMICAL TEST METHOD

A rapid chemical test method, as used at the Indiana Station, was tried in comparison with the Neubauer and the Fungus methods. In round numbers, the rapid method was in agreement with the Neubauer, on the basis of a simplified or 3-group standard, for  $P_2O_5$  in 60 per cent of the soil samples, and for  $K_2O$  in 67 per cent. In comparison with the Fungus tests, the rapid test gave a 60 per cent agreement for  $P_2O_5$  and a 75 per cent agreement for  $K_2O$ . The  $P_2O_5$  test by the rapid method was especially out of harmony with the others in the case of soils with medium or high content. On the other hand, the standing of the  $K_2O$  test by the rapid method was good at all levels.

## SOURCES OF ERROR IN THE NEUBAUER METHOD

No special study was made to account for the evident large error to which the Neubauer method is liable. Two sources are recognized. One is the large amount of  $P_2O_5$  and  $K_2O$  in the hundred seeds of rye sown in each trial. The  $P_2O_5$  content of the seed used was approximately 24 mg., equivalent to 480 pounds of  $P_2O_5$  per acre, or nearly 10 times the amount contained in an average soil; and the content of  $K_2O$  was approximately 16 mg. Variations in the individual lots of seed are common, however, and, for  $P_2O_5$ , may amount to 2 mg., or 40 pounds per acre. It is unfortunate that the exact allowances for the seed used cannot be known. The other source of error lies in the analytical process, and though this error may be small, it is a factor to be considered.

## COMPARATIVE ECONOMY OF THE NEUBAUER AND THE FUNGUS METHODS

With the Neubauer method, two men complete 48 soil samples a week. Ten times this number can be handled by the same force, using the Fungus methods. Also, the equipment for the Fungus methods is comparatively simple, whereas a fairly complete chemical laboratory is required for the Neubauer method. The time required for completion of a soil analysis is an item of importance; from the receipt of the soil sample to the rendering of a report, nearly 20 days would be needed for the Neubauer method as compared with only 3 or 4 days for the Fungus methods.

## SUMMARY

In a comparison of the Neubauer and the Fungus methods for the determination of the fertilizer needs of a soil, 129 samples of soil, representing 9 different soil types, 1 soil type phase, and 1 land type, were used.

The majority of the soil samples were obtained from experimental plots for many of which records of crop yields and fertilizer treatments were available for 25 or more years.

The Neubauer and the Fungus methods made positive distinctions between fertilized and unfertilized plots on the same kind of soil.

The comparative rating of various soil types by the Neubauer and the Fungus methods was, in the majority of cases, in general harmony with the

known condition of the soils. A marked exception was the low rating of Memphis silt loam by the Cunninghamella method as compared with the apparently proper rating by the Neubauer method. On the other hand the rating of a fertile Cumberland loam was appreciably more in harmony with crop production by the Cunninghamella method than by the Neubauer method.

The evidence was considered conclusive that different soils might require materially different standards of interpretation, and specific instances were pointed out.

Although there was a general agreement in the data obtained by the Neubauer and the Fungus methods when a number of samples could be averaged, there was frequent and wide disagreement in individual samples.

Standards of interpretation were set up for the purpose of a more specific comparison of the results obtained by the methods.

Cumberland loam samples from a long-continued series of fertilizer experiments furnished evidence as to the comparative liability to error of the methods, and the conclusion was reached that the Neubauer method for both  $P_2O_5$  and  $K_2O$  was liable to serious error in individual samples and that the Fungus methods were far superior in this respect because of their low inherent source of error.

The Neubauer and the Cunninghamella methods as means of obtaining an index of the availability of different phosphates for each of five types of soil were compared. For calcium metaphosphates, neither method gave results in harmony with the data from field experiments. The ranking of the other phosphates by the two methods was in wide disagreement, but that by the Cunninghamella method was in close harmony with the field results.

Trial was made of a rapid chemical test method as used at the Indiana Station. Results by the rapid method were in reasonable agreement with the Neubauer data for  $P_2O_5$  in 60 per cent of the soil samples, and for  $K_2O$  in 67 per cent. The agreement between the rapid test method and the Fungus methods was 60 per cent for  $P_2O_5$  and 75 per cent for  $K_2O$ . The rapid method for  $P_2O_5$  gave results especially out of harmony with the others in the case of soils of medium or high content. On the other hand, it gave good results for  $K_2O$  at all levels.

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# BEHAVIOR OF CALCIUM, MAGNESIUM, AND POTASSIUM SULFATES, AS INFLUENCED BY LIMESTONE AND BY DOLOMITE—A LYSIMETER STUDY

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In unfertilized soils, the plant is primarily dependent upon two sources of sulfates, those engendered within the soil, and those brought by rain waters (17, 20). It has been shown that rain waters bring sulfates of calcium, magnesium, and potassium to the soil, and that location, season, and proximity to coal-burning operations materially influence the amounts of these increments (6, 7, 14, 15, 17). Recently, however, Alway, Marsh, and Methley (1) demonstrate the infusion of atmospheric  $\text{SO}_2$  into the soil and cited four contributions relative to the inhalation of atmospheric sulfur dioxide by plants.

Since heavy fertilization has been common in those regions where several crops per annum are harvested, the amounts of sulfates supplied by superphosphate and by the potassium, magnesium, and ammonium sulfates of mixed fertilizers have probably provided ample quantities of nutrient sulfur. The increasing usage of phosphatic concentrates, however, has resulted in revived discussions and claims as to the adequacy of the sulfates supplied to crops by natural agencies.

## RELATED FINDINGS

Some of the residual effects of ammonium sulfate and calcium sulfate in the soil of the Jordan Fertility Plots have been determined (3, 4, 24). Little is known, however, as to any differential effect that variation in cation combination of the  $\text{SO}_4$  of sulfate additions may exert upon (a) conservation of sulfates in the soil, and (b) extent of interchange reactions, as registered by altered outgo of bases.

Previous lysimeter studies have indicated that a near-balance exists between the amounts of sulfates brought to unlimed fallow soils and those leached from such soils (2, 6, 7, 14, 15, 17), that the intensity of the initial accelerative effect of economic liming treatments upon sulfate outgo is not sustained (2, 6, 7, 17), and that clay subsoils have a retentive capacity for the sulfates that leach from overlying soils (2, 14, 19).

Although magnesium sulfate is much more soluble than calcium sulfate, the behavior of additions of the more soluble sulfate to soils of the humid region is influenced by the content of exchangeable calcium, which usually exceeds



the content of exchangeable magnesium. Hence, when one of these two sulfates is added to the soil, the proportion that leaches in the form applied and the proportion that enters into the soil system through exchange reactions, are governed by those variables. The differential effects of lime and magnesia upon sulfate generation and outgo are known (8, 14, 15, 17, 19). Although soil-engendered sulfates may exert little effect on potassium outgo (13, 15, 17), a portion of the potassium added as sulfate may be fixed in an exchangeable form, whereas another portion may be so tenaciously held as to resist rigorous chemical extractions (22).

#### OBJECTIVES

The present lysimeter experiment was initiated to study the fate of annual equivalent incorporations of calcium, magnesium, and potassium sulfates. The three principle objectives were to determine (a) whether the cation combination influences the conservation of added  $\text{SO}_4$ , (b) the nature and extent of interchange reactions induced by each of the three sulfates, and (c) any divergent influence that single economic incorporations of limestone and of dolomite exert on (a) and (b).

TABLE 1

*Analyses of the brown clay loam used in the study of the history of annual equivalent additions of sulfates of calcium, magnesium, and potassium*

SULFUR AS $\text{CaSO}_4$ $\infty$		REPLACEABLE BASES†			NITROGEN
Total*	Water-soluble	CaO	MgO	K <sub>2</sub> O	
per cent	per cent	per cent	per cent	per cent	per cent
0.212	0.019	0.192	0.036	0.081	0.204

\*  $\text{Na}_2\text{CO}_3$ — $\text{Na}_2\text{O}_2$  fusion (10).

† By boiling 0.1 N  $\text{NH}_4\text{Cl}$  (12).

#### EXPERIMENTAL

The soil used was a brown silty clay loam that had been in sod for many years and was unusually rich in exchangeable bases and organic matter (table 1). The sod was skimmed off and discarded. The soil had an initial pH of 6.77, which rose to 6.89 after aqueous leaching. Seven annual full-depth incorporations of each of the three sulfates were made, at the equivalent-rate of 400 pounds of calcium sulfate per 2,000,000 pounds of surface soil, in asphaltum-coated outdoor lysimeters having an area of 1/20,000 acre. The metal surface of the leachate receptacles were likewise protected by an asphaltum coating. Annual incorporations of potassium sulfate were also made at the  $\text{CaSO}_4$ -equivalent rate of 800 pounds. The untreated control soils were also worked when the annual incorporations of sulfates were made. Single full-depth incorporations of limestone and of dolomite, both of 100 mesh, were also included as initial supplements to the several sulfates, both supplements being at the equivalent-rate of 2 tons of  $\text{CaCO}_3$  per 2,000,000 pounds of soil. The total sulfur content of the limestone supplement was equivalent to only 1.7 pounds

of  $\text{CaSO}_4$ ; but, because of its content of zinc sulfide as sphalerite, the supplement of dolomite introduced the equivalence of 55 pounds of  $\text{CaSO}_4$ . The rain waters were collected at each end of the lysimeter installation. The collections of the rain waters and leachates of each annual period were brought to composite acidic solutions in glass containers, and the  $\text{SO}_4$ , calcium, magnesium, and potassium contents of each annual composite were determined.

### *Sulfate conservation*

Expressed as  $\text{CaSO}_4$ , the sulfate contents of the rain waters and of the leachates from each soil treatment are given, in table 2, for the seven annual periods. The increments of sulfates brought to the soil by rain waters show the usual variation ascribed to extent and proximity of coal consumption and also to location of receptacles. Any variations in sulfate increment are obliterated, however, during the passage of the rain waters through the untreated soil. Since the rain waters were caught in receptacles and collected in containers that were asphaltum-coated, the point raised by Alway, Marsh, and Methley (1) as to the action of atmospheric  $\text{SO}_2$  upon the surface of galvanized iron does not apply to the rain waters and leachates of the present experiment.

To determine the respective recoveries from the three added sulfates, the mean outgo from the untreated units was deducted from each 7-year outgo from the 2,800-pound and 5,600-pound sulfate treatments.

Complete  $\text{SO}_4$  recoveries were obtained only from the 2,800-pound-rate additions of magnesium and potassium sulfates, incorporated with the dolomitic supplement. If the 55-pound sulfate-equivalent of the sphalerite content of the dolomite were counted as a potential sulfate addition, however, these two complete recoveries would be reduced to recoveries of 98 per cent. The mean conservation of 4.3 per cent found for the other seven sulfate treatments of 400 pounds each per annum was, however, equivalent to 120 pounds of calcium sulfate.

No repressive effect upon the outgo of sulfates from the calcium sulfate addition was induced by the 2-ton supplement of either limestone or dolomite. The two types of limestone likewise failed to repress outgo of sulfates from the additions of magnesium sulfate. The difference in solubilities of the two sulfates is minimized in the rainwater leachings, the mean recoveries of  $\text{SO}_4$  from the calcium sulfate and magnesium sulfate additions being 95.4 per cent and 97.1 per cent, respectively. In previous studies where no sulfates were added, additions of magnesian materials caused a greater outgo of sulfates. This was attributed to a larger supply of sulfates resultant from the greater accelerative effect of magnesia upon sulfonation (6, 14, 15, 19).

The sulfate outgo from the unsupplemented potassium sulfate additions at the 400-pound rate was substantially the same as the sulfate outgo from the unsupplemented additions of calcium and magnesium sulfates. Both limestone and dolomite induced increases in sulfate outgo from the potassium sulfate additions at the 400-pound rate, and respective recoveries of 99 and

TABLE 2

*Outgo of sulfates from seven annual equivalent additions of calcium, magnesium, and potassium sulfates, with and without limestone and dolomite*

TANK NUMBER	TREATMENT	SULFATE OUTGO, IN TERMS OF POUNDS OF CaSO <sub>4</sub> PER 2,000,000 POUNDS OF SOIL									
		1930-31	1931-32	1932-33	1933-34	1934-35	1935-36	1936-37	1930-1937		
									Total	Derived from addi- tion*	
	Annual sulfate additions, in terms of 400 pounds CaSO <sub>4</sub> ∞	Single initial addition ≈ 2 tons of CaCO <sub>3</sub>									Per cent
617	Rainwater	None	124	102	90	71	90	110	106	693	..
618	None	None	312	341	218	160	230	224	161	1,646	..
619	CaSO <sub>4</sub>	None	642	694	599	514	672	640	506	4,267	93.7
20	CaSO <sub>4</sub>	Limestone	739	690	596	582	621	625	531	4,384	97.9
21	CaSO <sub>4</sub>	Dolomite	749	690†	566	594	551	620	518	4,288	94.5
622	MgSO <sub>4</sub>	None	671	750	571	489	665	631	536	4,313	95.4
23	MgSO <sub>4</sub>	Limestone	757	649	570	545	641	620	547	4,329	95.9
24	MgSO <sub>4</sub>	Dolomite	774	742	591	536	635	600	564	4,442	100.0
625	K <sub>2</sub> SO <sub>4</sub>	None	670	747	582	466	666	609	517	4,257	93.4
26	K <sub>2</sub> SO <sub>4</sub>	Limestone	763	712	634	540	649	582	534	4,414	99.0
27	K <sub>2</sub> SO <sub>4</sub>	Dolomite	760	773	608	534	642	611	517	4,445	100.1
28	2 × K <sub>2</sub> SO <sub>4</sub>	None	1,036	1,059	978	831	1,071	983	910	6,868	93.3
29	2 × K <sub>2</sub> SO <sub>4</sub>	Limestone	1,173	1,054	978	914	1,015	1,001	869	7,004	95.7
30	2 × K <sub>2</sub> SO <sub>4</sub>	Dolomite	1,168	1,049	1,013	761	1,037	982	880	6,890	93.7
631	None	None	307	347	220	154	231	211	170	1,640	....
632	Rainwater	None	81	88	76	58	80	96	105	584	....
Inches of rainfall			38.83	55.33	55.95	38.45‡	61.77	47.23§	52.05	349.6	....

\* Total additions of 2,800 pounds and 5,600 pounds CaSO<sub>4</sub> or equivalent.

† Computed.

‡ An additional collection of 12.16 inches was made in rain gauges during a period when the tanks were covered.

§ An additional collection of 2.35 inches was made in rain gauges during a period when the tanks were covered.

100 per cent. As noted, however, the latter value would be reduced to 98.1 per cent, were the sulfate-equivalent of the sphalerite content of the dolomite computed as an additive treatment. The recovery of  $\text{SO}_4$  from the unsupplemented additions of  $\text{K}_2\text{SO}_4$  at the double rate of 800 pounds was almost identically proportionate to the recovery of  $\text{SO}_4$  from the 400-pound additions. Neither limestone nor dolomite showed any material influence upon the conservation of sulfates from the double, or 800-pound, annual addition of  $\text{K}_2\text{SO}_4$ .

### *Outgo of calcium*

The amounts of calcium, in terms of  $\text{CaCO}_3$ , that passed from the controls and from different treatments during the 7 year period are shown in table 3.

The outgo of calcium from the unsupplemented calcium sulfate addition was virtually identical with that found for the same addition with its dolomitic supplement. This is in accord with previous findings to the effect that the outgo of calcium from clay loam soils may not be enhanced by economic additions of dolomite (16), at least for several years, a result that is reflected in the composition of plant growth. The mean of increases in calcium outgo from the calcium sulfate additions, alone and also with dolomite, represents only 68 per cent of the amounts of calcium supplied by the added calcium sulfate.

Each year, and especially during the first two years, the maximal outgo of calcium from the calcium sulfate series was induced by the limestone supplement. If the entire amount of calcium added as sulfate was removed by leaching, as was indicated by the 98 per cent recovery of  $\text{SO}_4$ , the increase in the mean annual  $\text{CaCO}_3$ -equivalent outgo of calcium derived from the 2-ton limestone supplement was only 167 pounds. The increase in calcium outgo induced by the limestone supplement was somewhat greater in its association with the sulfate of calcium than with the other two sulfates.

The additions of magnesium sulfate induced exchange reactions that caused a substantial increase in the outgo of calcium from the unlimed soil. Magnitude of increases in calcium outgo from this series was in the ascendant order, sulfate alone, sulfate + dolomite, and sulfate + limestone. The increased outgo of calcium induced by the limestone supplement, in its association with the seven annual additions of magnesium sulfate, was approximately 1,000 pounds less than the outgo of calcium induced by the limestone in its association with calcium sulfate. The increase in calcium outgo attributable to the dolomite supplement was only 146 pounds for the 7-year period. It is evident that the additions of magnesium sulfate replaced a considerable quantity of the native calcium and also effected some exchange for the supplies of sorbed calcium, unless the magnesium sulfate additions caused more of the calcium content of the rainwaters to pass through the soil. If the 78-pound per annum increase in calcium outgo from the seven unsupplemented annual incorporations of magnesium sulfate is attributed solely to exchange reactions, then the extent of such reactions was only one fourth of the potential exchange capacity of the added magnesium sulfate.

TABLE 3  
*Outgo of calcium as influenced by seven annual equivalent incorporations of sulfates of calcium, magnesium, and potassium\**

CALCIUM LEACHED, IN TERMS OF POUNDS $\text{CaCO}_3$ PER 2,000,000 POUNDS OF SOIL											
TANK NUMBER	TREATMENT		1930-31	1931-32	1932-33	1933-34	1934-35	1935-36	1936-37	1930-1937	
	Annual sulfate additions, in terms of 400 pounds $\text{CaSO}_4 \rightleftharpoons$	Single initial addition $\rightleftharpoons$ 2 tons of $\text{CaCO}_3$								Total	Increase Annual
617	Rainwater	None	264	209	172	153	149	138	183	1,268	.
618	None	None	495	609	446	463	386	456	292	3,147	.
619	$\text{CaSO}_4$	None	650	700	582	632	649	674	461	4,348	1,314
20	$\text{CaSO}_4$	Limestone	945	936	774	723	734	806	604	5,522	2,488
21	$\text{CaSO}_4$	Dolomite	717	748	599	600	546	635	505	4,350	1,316
622	$\text{MgSO}_4$	None	603	660	473	454	476	549	366	3,581	547
23	$\text{MgSO}_4$	Limestone	921	656	686	608	582	602	472	4,527	1,493
24	$\text{MgSO}_4$	Dolomite	727	693	575	409	476	461	386	3,727	693
625	$\text{K}_2\text{SO}_4$	None	589	658	501	447	403	434	332	3,364	330
26	$\text{K}_2\text{SO}_4$	Limestone	927	796	682	561	553	529	413	4,461	1,427
27	$\text{K}_2\text{SO}_4$	Dolomite	653	690	497	438	453	456	336	3,523	489
628	$2 \times \text{K}_2\text{SO}_4$	None	645	669	603	495	475	441	376	3,704	670
29	$2 \times \text{K}_2\text{SO}_4$	Limestone	1,110	902	712	630	522	539	392	4,807	1,773
30	$2 \times \text{K}_2\text{SO}_4$	Dolomite	799	692	616	346	450	451	338	3,692	253 [157]
631	None	None	449	549	438	404	371	446	263	2,920	94 [-2]
632	Rainwater	None	138	126	140	104	112	121	140	881	....
Inches of rainfall.....			38.83	55.33	55.95	38.45†	61.77	47.23‡	52.05	349.6	....

\* Total additions of 2,800 pounds and 5,600 pounds  $\text{CaSO}_4$  or equivalent.

† Bracketed figures show the increases attributable to either limestone or dolomite.

‡ An additional collection of 12.16 inches was made in rain gauges during a period when the tanks were covered.

§ An additional collection of 2.35 inches was made in rain gauges during a period when the tanks were covered.

If the enhancement in calcium outgo induced by the seven unsupplemented annual additions of potassium sulfate at the 400-pound rate is a true index of the replacement of Ca by K, the sulfate functioned to only 32 per cent of its potential exchange capacity. The corresponding enhancement in calcium outgo induced by the unsupplemented 5,600-pound total of added  $K_2SO_4$  was practically double the enhancement in calcium outgo from the 2,800-pound aggregate. The two rates of potassium sulfate gave almost identical increases, however, in the calcium outgo computed as attributable to the limestone supplement. Since related studies have demonstrated that the 2-ton addition of the fine limestone and its dolomite equivalent probably entered the soil complex during the first year (11), the amounts of replaceable calcium subject to the action of the added  $K_2SO_4$  were consequently greater in the soil that that received the liming supplements. More extensive exchange and greater outgo of calcium would, therefore, be expected from the double quantity of  $K_2SO_4$  in the soil systems enriched by sorbed calcium derived from the supplements of limestone and dolomite. When acting upon increased amounts of calcium supplied by the limestone and the dolomite, the double  $K_2SO_4$  additions did increase the outgo of calcium above that induced by the 400-pound additions, but the double additions also increased by 100 per cent the outgo of calcium from the control, and there was, therefore, no net increase in outgo of calcium from the liming treatments. Hence, when acting *solely* upon native supplies of soluble and exchangeable forms of calcium, the double additions of  $K_2SO_4$  were doubly effective in causing a limited exchange of K for Ca. When the native supplies of replaceable Ca had been augmented, however, by the sorbed Ca derived from either of the two liming materials, the double additions of potassium sulfate fell far short of exerting their potential capacity to effect exchange reactions with the calcium components of the soil.

The actual differences between total calcium outgo from the unsupplemented additions of the sulfates of calcium, magnesium, and potassium, and from the same three sulfates with limestone supplements were 1,174, 946, and 1,097 pounds respectively for the 7-year period.

#### *Outgo of magnesium*

The magnesium data, in terms of  $CaCO_3$ , are given in table 4. The total displacement of magnesium by additions of calcium sulfate was only 186 pounds for the 7-year period, or 27 pounds per annum. This replacement was only about one-third of the reciprocal replacement of calcium by the magnesium sulfate treatments (table 3) and was equivalent to only 9 per cent of the potential exchange capacity of the added calcium sulfate. But, the supplement of limestone completely nullified the potential capacity of the added calcium sulfate to replace magnesium and also potassium (table 5).

The recovery of the magnesium from the unsupplemented additions of magnesium sulfate was 60 per cent of the amount added. The effect of the limestone supplement, was to reduce that recovery to 40 per cent of the added

TABLE 4  
*Outgo of magnesium as influenced by seven annual equivalent incorporations of sulfates of calcium, magnesium, and potassium\**

TANK NUMBER	TREATMENT		MAGNESIUM LEACHED, IN TERMS OF POUNDS $\text{CaCO}_3$ PER 2,000,000 POUNDS OF SOIL									
	Annual sulfate additions, in terms of 400 pounds $\text{CaSO}_4 \approx$	Single initial addition $\approx$ 2 tons of $\text{CaCO}_3$	1930-31	1931-32	1932-33	1933-34	1934-35	1935-36	1936-37	1930-1937		
			Total outgo	Increase	Annual							
617	Rainwater	None	38	46	67	36	48	47	57	339	...	
618	None	None	249	305	217	178	141	162	103	1,355	...	
619	$\text{CaSO}_4$	None	330	333	245	188	166	168	104	1,534	27	
20	$\text{CaSO}_4$	Limestone	272	270	211	161	154	160	118	1,346	0 [0]†	
21	$\text{CaSO}_4$	Dolomite	505	510	399	338	256	278	193	2,479	161 [134]	
622	$\text{MgSO}_4$	None	390	401	365	332	356	438	295	2,577	167	
23	$\text{MgSO}_4$	Limestone	333	242	327	302	304	361	296	2,165	117 [-50]	
24	$\text{MgSO}_4$	Dolomite	608	629	573	381	430	466	361	3,448	300 [133]	
625	$\text{K}_2\text{SO}_4$	None	311	344	238	171	140	149	111	1,464	17	
26	$\text{K}_2\text{SO}_4$	Limestone	282	260	213	149	139	148	106	1,297	-7 [0]	
27	$\text{K}_2\text{SO}_4$	Dolomite	488	604	381	292	260	269	185	2,479	161 [144]	
628	$2 \times \text{K}_2\text{SO}_4$	None	343	352	277	181	149	148	121	1,571	32	
29	$2 \times \text{K}_2\text{SO}_4$	Limestone	335	283	228	159	131	154	104	1,394	46	
30	$2 \times \text{K}_2\text{SO}_4$	Dolomite	599	578	457	223	253	247	176	2,533	7 [0]	
631	None	None	253	301	221	162	138	167	98	1,340	169 [137]	
632	Rainwater	None	35	42	72	34	37	36	44	300	...	
Inches of rainfall.....			38.83	55.33	55.95	38.45†	61.77	47.23‡	52.06	349.6	...	

\* Total additions of 2,800 pounds and 5,600 pounds  $\text{CaSO}_4$  or equivalent.

† Bracketed figures show the increases attributable to either limestone or dolomite.

‡ An additional collection of 12.16 inches was made in rain gauges during a period when the tanks were covered.

§ An additional collection of 2.35 inches was made in rain gauges during a period when the tanks were covered.

magnesium. In contrast, the dolomite supplement induced an 871-pound increase in total magnesium outgo. Full recovery of the magnesium supplied as the sulfate was obtained only in its association with the dolomitic supplement and, with the 2,100-pound increase in magnesium outgo, there was a concomitant increase of 693 pounds in calcium outgo.

The replacement-outgo of magnesium induced by the 2,800-pound potassium sulfate treatment was less than 6 per cent of its potential exchange capacity. Again, as in the calcium sulfate series, the limestone supplement nullified the potential capacity of this potassium sulfate treatment to release magnesium, and an exchange of only 46 pounds was registered by the double treatment of 5,600 pounds. The outgo of magnesium induced by the 2,800-pound aggregate of the potassium sulfate additions and its supplement of dolomite was identical with that induced by the equivalent additions of calcium sulfate and dolomite, whereas the additional 2,800-pounds of potassium sulfate induced a further increase of only 54 pounds in magnesium outgo. It is evident that the added potassium ions did not release an equivalence of magnesium, or of calcium, or even of  $\text{Ca} + \text{Mg}$ . This follows also from data of table 5 that show that the maximal retentions of K were only 42 per cent and 36 per cent respectively for the single- and double-rate additions of potassium sulfate.

*Influence of the three added sulfates upon the Ca:Mg ratio in leachings*

The Ca:Mg ratio in the leachates from the untreated soil was 2.25 to 1. In the total  $\text{Ca} + \text{Mg}$  outgo of 5,882 pounds of  $\text{CaCO}_3$ -equivalence from the unsupplemented calcium sulfate additions, the ratio of Ca to Mg was 2.8:1. For the total  $\text{Ca} + \text{Mg}$  outgo of 6,868 pounds from the  $\text{CaSO}_4$ + limestone treatment, the Ca:Mg ratio was 4.1:1, as against 1.8:1 for the 6,829-pound total outgo of  $\text{Ca} + \text{Mg}$  from the calcium sulfate and its dolomitic supplement.

Since the outgo of magnesium from the combination treatment of calcium sulfate and limestone was the same as the magnesium outgo from the untreated soil, the enhancement of 2,486 pounds in outgo of calcium alone from that combination was identical to the enhancement in outgo of  $\text{Ca} + \text{Mg}$ . The enhanced outgo of  $\text{Ca} + \text{Mg}$  for the corresponding calcium sulfate + dolomite system was 2,447 pounds, of which 54 per cent was accounted for by calcium and 46 per cent by magnesium.

For the magnesium sulfate series, the Ca:Mg ratio obtained in the 6,158-pound total outgo from the unsupplemented sulfate was 1.4:1. It was 2.1:1 in the 6,692-pound total outgo from the magnesium sulfate with the limestone supplement, and it was 1.1:1 in the 7,175-pound total outgo from the combination treatments of magnesium sulfate and dolomite. The Ca:Mg relationships for the enhancements in outgo induced by the magnesium sulfate in the limestone and dolomite systems were, therefore, 1.8:1 and 1:3 respectively.

The supplements of both limestone and dolomite caused increases of approximately 1,000 pounds in the outgo of  $\text{Ca} + \text{Mg}$  from the calcium sulfate treatment. The dolomitic limestone also increased the  $\text{Ca} + \text{Mg}$  outgo approx-



imately 1,000 pounds above that from the unsupplemented magnesium sulfate. Because of the repressive effect of the limestone upon outgo of magnesium, however, the enhancement in Ca + Mg outgo from the magnesium sulfate and its limestone supplement was restricted by about one-half.

In the Ca + Mg outgo of 4,728 pounds and that of 5,275 pounds from the 2,800-pound and 5,600-pound unsupplemented potassium sulfate additions, the respective Ca:Mg ratios were 2.3:1 and 2.4:1. When supplemented with limestone, the two rates of  $K_2SO_4$  gave Ca + Mg outgo totals of 5,767 pounds and 6,201 pounds, in both of which the Ca:Mg ratio was 3.4:1. For the supplements of dolomite, the totals of Ca + Mg outgo from the two rates of  $K_2SO_4$  were 6,002 pounds and 6,225 pounds, with respective Ca:Mg ratios of 1.42:1 and 1.45:1.

The enhancement in Ca + Mg leached from the dolomitic supplement to the seven 400-pound-rate additions of  $K_2SO_4$  was 1,620 pounds, of which calcium and magnesium were responsible for respective fractions of 30 per cent and 70 per cent. Of the total enhancement of 1,843 pounds in Ca + Mg outgo from the seven double-rate  $K_2SO_4$  additions with the dolomitic supplement, Ca and Mg accounted for 36 per cent and 64 per cent, respectively. Although each double potassium sulfate treatment induced some further increases in outgo of Ca + Mg from the liming supplements, the increases were not proportionate to the potential exchange capacity of the double additions.

#### *Outgo of potassium*

The potassium contents of the rainwaters and the amounts of K leached, per 2,000,000 pounds of soil, are given in table 5. At the two rates, the potassium sulfate supplied 1,608 pounds and 3,216 pounds of K, or annual additions of 230 pounds and 460 pounds. The accumulation of exchangeable potassic compounds that developed during the previous period of sod culture and the biochemical activities that ensued when the sod-denuded soil was maintained fallow, are reflected by the unusually high concentration of potassium in the leachates from the untreated controls, especially during the initial 2-year period. After years of cultivation, the same type of soil, without potash treatment, yielded only about 5-10 pounds of K per annum to the leachates (5, 13, 18).

Although ground gypsum, or land plaster, is now seldom added as a separate soil treatment, its use has been advocated and practiced in certain sections. It was one of the treatments applied to the Jordan Fertility Plots (3), initiated in 1881. Storer (23, p. 325) stated, "This substance has been used as a fertilizer from time immemorial." He and Patten (21) believed that it effected liberation of soil potash.

None of the three treatments of calcium sulfate, alone and with supplements of limestone and dolomite, caused an increase in the outgo of K from this slightly acidic soil of high content of readily leached K. Nevertheless, a 4,250-pound equivalence of calcium sulfate, engendered within the soil from addi-

tions of ferrous sulfate, did effect a meager release of K from the same type of soil, when more acidic and of depleted exchangeable K content (15). In that experiment, liming materials also completely nullified the potential capacity of the engendered calcium sulfate to effect an exchange for potassium, as reflected by a decrease in the outgo of potassium. It appears, therefore, that additions of calcium and magnesium sulfates *cannot* be depended upon to

TABLE 5

*Outgo of potassium, as influenced by seven annual equivalent incorporations of sulfates of calcium, magnesium, and potassium\**

TANK NUMBER	TREATMENT		POTASSIUM LEACHED, IN TERMS OF POUNDS K PER 2,000,000 POUNDS OF SOIL								1930-1937		
	Annual sulfate additions, in terms of 400 pounds $\text{CaSO}_4$ or	Single initial addition $\approx$ 2 tons of $\text{CaCO}_3$	1930-31	1931-32	1932-33	1933-34	1934-35	1935-36	1936-37	Total outgo	Increase		
											Total	Annual	
517	Rainwater	None	7	5	5	3	5	6	6	37	.....	...	
518	None	None	103	107	74	41	55	45	24	449	.....	...	
519	$\text{CaSO}_4$	None	114	106	72	35	55	45	24	451	-8	-1	
20	$\text{CaSO}_4$	Limestone	106	104	66	32	52	45	27	432	-27	-4	
21	$\text{CaSO}_4$	Dolomite	93	104	62	34	47	48	27	415	-44	-6	
522	$\text{MgSO}_4$	None	112	110	76	35	54	45	27	459	0	0	
23	$\text{MgSO}_4$	Limestone	105	91	65	34	45	56	27	423	-36	-5	
24	$\text{MgSO}_4$	Dolomite	104	105	68	29	46	46	27	425	-34	-5	
525	$\text{K}_2\text{SO}_4$	None	160	235	273	149	255	253	184	1,509	1,050	150	
26	$\text{K}_2\text{SO}_4$	Limestone	151	191	231	137	249	255	191	1,405	946	135	
27	$\text{K}_2\text{SO}_4$	Dolomite	135	220	232	145	217	263	180	1,392	933	133	
528	$2 \times \text{K}_2\text{SO}_4$	None	247	376	386	341	484	466	342	2,642	2,183	312	
29	$2 \times \text{K}_2\text{SO}_4$	Limestone	260	313	402	304	443	456	354	2,532	2,073	296	
30	$2 \times \text{K}_2\text{SO}_4$	Dolomite	245	354	430	249	466	457	369	2,570	2,111	302	
531	None	None	98	106	89	43	53	54	26	469	.....	...	
532	Rainwater	None	6	5	5	4	5	5	5	35	.....	...	
Inches of rainfall .....			38.83	55.33	55.95	38.45†	61.77	47.23†	52.05	349.6	.....	...	

\* Total additions of 2,800 pounds and 5,600 pounds  $\text{CaSO}_4$  or equivalent.

† An additional collection of 12.46 inches was made in rain gauges during a period when the tanks were covered.

‡ An additional collection of 3.25 inches was made in rain gauges during a period when the tanks were covered.

effect an enrichment in supplies of nutrient potassium by direct chemical reactions, especially on either naturally calcareous or limed soils.

Taken in connection with the results of table 2, the data of table 5 show that the additions of potassium sulfate were leached mainly in that form. The increases in the amounts of K leached from the unsupplemented 2,800-pound and 5,600-pound  $\text{CaSO}_4$ -equivalent additions of potassium sulfate were 65 and

68 per cent of the respective amounts incorporated. The recoveries of K from the two corresponding cumulative additions of potassium sulfate with limestone supplements were 59 per cent and 64 per cent, whereas respective K recoveries of 58 per cent and 66 per cent were obtained when dolomitic supplements were used. For additions of potassium sulfate at both rates, the outgo of potassium was therefore decreased somewhat by both types of lime-

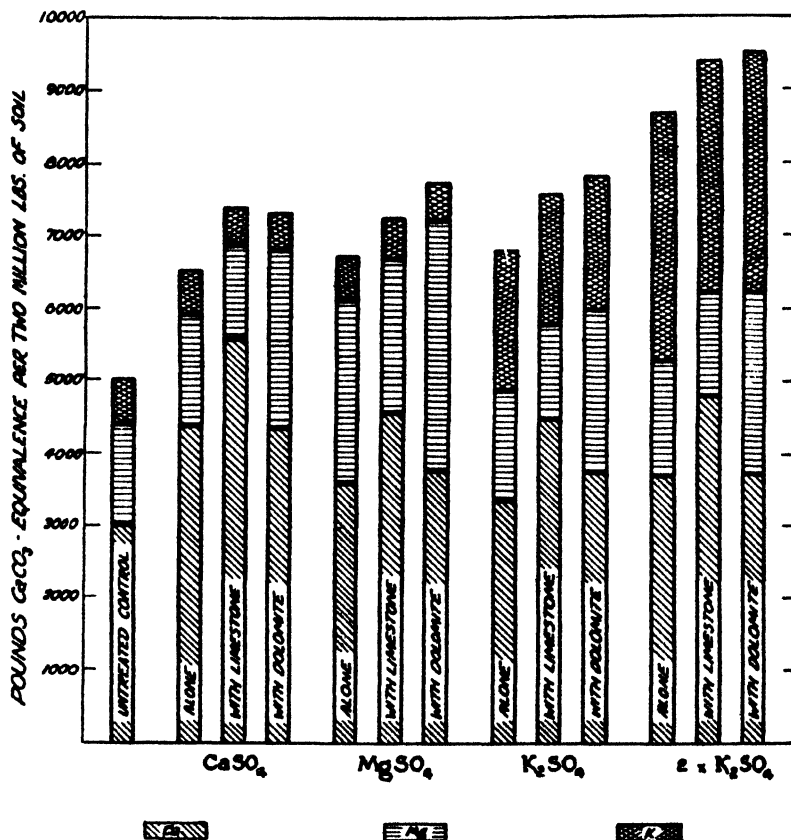


FIG. 1. OUTGO OF CALCIUM, MAGNESIUM, AND POTASSIUM FROM A SOD-SKIMMED SOIL TREATED WITH SEVEN ANNUAL EQUIVALENT INCORPORATIONS OF SULFATES OF CALCIUM, MAGNESIUM, AND POTASSIUM, WITH AND WITHOUT A SINGLE INITIAL ADDITION OF EITHER LIMESTONE OR DOLOMITE

stone. It has been shown that the repressive effect exerted by liming materials upon K outgo is much more pronounced when light additions of K are made (9).

#### *Outgo of total bases induced by the three sulfates*

The results of table 6 show the respective aggregates for outgo of "total bases"—calcium, magnesium, and potassium. To allow direct additive values, in terms of pounds per 2,000,000 pounds of soil in this table outgo of

potassium was computed to the  $\text{CaCO}_3$ -equivalence values, as was done for the outgo of calcium and of magnesium in tables 3 and 4, respectively.

The  $\text{CaCO}_3$ -equivalence of the aggregate of the seven additions of each of the three sulfates at the 400-pound rate was 2,059 pounds. The  $\text{SO}_4$  data of table 2 showed that the  $\text{SO}_4$  recoveries from the three sulfates were in the range of 93–100 per cent. A cation build-up from each of the sulfates occurred, since the enhancements in outgo of total bases from the unsupplemented additions of calcium and magnesium sulfates, and also of potassium sulfate at

TABLE 6

*Effect of calcium, magnesium, and potassium sulfate treatments, with and without limestone and dolomite, on total bases\* leached during the 7-year period*

TANK NUMBER	TREATMENT		Ca, Mg, AND K, EXPRESSED AS $\text{CaCO}_3$ $\infty$ , POUNDS PER 2,000,000 POUNDS OF SOIL				
	Annual sulfate additions, in terms of 400 pounds $\text{CaSO}_4 \infty$	Single initial additions $\infty$ 2 tons of $\text{CaCO}_3$	Calcium	Magne- sium	Potas- sium	Aggregate	Increase†
618	None	None	3,147	1,355	575	5,077	.....
619	$\text{CaSO}_4$	None	4,348	1,534	577	6,459	1,490
20	$\text{CaSO}_4$	Limestone	5,522	1,346	553	7,421	2,452
21	$\text{CaSO}_4$	Dolomite	4,350	2,479	531	7,360	2,391
622	$\text{MgSO}_4$	None	3,581	2,577	588	6,746	1,777
23	$\text{MgSO}_4$	Limestone	4,527	2,165	541	7,233	2,264
24	$\text{MgSO}_4$	Dolomite	3,727	3,448	544	7,719	2,750
625	$\text{K}_2\text{SO}_4$	None	3,364	1,464	1,932	6,760	1,791
26	$\text{K}_2\text{SO}_4$	Limestone	4,461	1,297	1,798	7,556	2,587
27	$\text{K}_2\text{SO}_4$	Dolomite	3,523	2,479	1,782	7,784	2,815
628	$2 \times \text{K}_2\text{SO}_4$	None	3,704	1,571	3,382	8,657	3,688
29	$2 \times \text{K}_2\text{SO}_4$	Limestone	4,807	1,394	3,241	9,442	4,473
30	$2 \times \text{K}_2\text{SO}_4$	Dolomite	3,692	2,533	3,290	9,515	4,546
631	None	None	2,920	1,340	600	4,860	.....

\* Related studies had demonstrated that the outgo of sodium native to the soil was so nugatory as to warrant its exclusion in the present study.

† By subtraction of mean outgo from controls, as result of a total rainfall of 349.6 inches.

both rates, were less than the respective  $\text{CaCO}_3$ -equivalences of the added sulfates. The enhancement in outgo of total bases from each limed unit was, however, in excess of the equivalence of the base carried by its companion sulfate treatment. In general, the greater solubility and mobility of the incorporations of magnesium sulfate was in evidence.

*The effect of residues of liming materials on conservation of subsequent additions of potassium sulfate*

In the study from which the data of tables 1–6 were obtained, the maximal effect of the full-depth incorporations of limestone and of dolomite were brought to bear upon soil naturally rich in readily soluble native salts, augmented by the annual incorporations of sulfates. In another and older lysim

eter experiment, the outgo of sulfates induced by 2,000-pound CaO-equivalent-rate additions of limestone, dolomite, burnt lime, and magnesia had been determined for a 12-year period (17). The two oxides had also been incorporated at the 3,750-pound rate.

Beginning with the thirteenth year after the liming treatments, annual surface additions of an aqueous solution of potassium sulfate were made to the fallow soils. These additions brought an annual supply of 68 pounds of sulfate sulfur. Certain units had also received single additions of sulfur, as ferrous sulfate, as pyrite, and as elemental sulfur, at the rate of 1,000 pounds of S. The balance between sulfur increment and outgo was reported in terms of S (15), and that expression is therefore continued in the data of table 7. The fate of the potassium supplied by the eight annual additions of potassium sulfate and the correlary record of outgo of Ca and Mg have been presented in a recent contribution (18). Since the fate of the  $\text{SO}_4$  radical of added sulfates is a primary consideration of the present paper, the reciprocal relationships between Ca, Mg, and K of the 20-year study will not be considered.

The data of table 7 show the accelerative effects of the several liming treatments upon total sulfate sulfur outgo during the initial 12-year period, 1917-1929, that preceded the 8-year period of annual additions of potassium sulfate. The magnesian materials were more accelerative than the calcic materials upon sulfate outgo. These increases of the initial 12-year period are attributable either to greater quantities of engendered sulfates, or to a change in soil structure that admitted of a more ready leaching of sulfates from a common supply of soil sulfates and rain water and atmospheric increments, or to combinations of these causes. Since the initial accelerative effect of the liming treatments had been diminished by the end of the twelfth year, the continued effect exerted by the residues of the liming materials upon retention of the added sulfates is probably due to altered capacities of the soils to retain sulfates.

Without exception, the amount of sulfate sulfur leached during the final 8-year period was greater than the 544-pound supply of S furnished solely by the eight additions of potassium sulfate. An additional common 326-pound increment from rain water, however, cannot be disregarded. Hence, each sulfate outgo was less than the amount of sulfates that entered the soil during the last 8 years.

The total amount of S leached from the unlimed soil was 79 per cent of the total increment from additions and rain water. Each liming treatment caused an enhancement in sulfate outgo within the range of 83 to 87 per cent of the common total increment. The enhancements in sulfate outgo attributable to the several liming materials were in the range of 6 to 14 per cent of the uniform amount of  $\text{SO}_4$  supplied by the eight annual additions of potassium sulfate, the magnesian materials being somewhat more accelerative than the calcic materials.

As noted, the accelerative effect that the liming materials exerted upon sulfication was most noticeable during the early years and had been sub-

TABLE 7  
*Outgo of sulfate sulfur induced by liming treatments and by subsequent annual additions of potassium sulfate\* from a clay loam during a 20-year period*

TANK NUMBER	FULL DEPTH SINGLE INCOR- PORATION 1917	OUTGO OF SULFATES, AS POUNDS S PER 2,000,000 POUNDS OF SOIL											
		From 8 annual additions of 200 pounds $K_2SO_4$ , 1929-1937											
		No sulfates added, period 1917-1929		1929-30		1930-31		1931-32		1932-33		1933-34	
		Actual outgo	Increase from soil, due to liming treat- ment	63	55	114	97	67	104	109	76	685	79
50	None	405	...	78	75	108	97	77	109	96	78	718	83
51	Limestone†	472	67	84	75	114	96	78	108	102	89	746	86
52	Dolomite‡	507	102	80	70	117	94	77	105	102	90	735	84
53	Burnt lime‡	503	98	87	82	110	93	84	98	101	91	746	86
54	Burnt lime§	524	119	85	72	115	92	77	104	100	91	736	84
55	MgO‡	494	89	92	88	112	91	87	100	99	92	761	87
56	MgO§	536	131										

\* Annual surface application, by solution, at the rate of 200 pounds  $K_2O$  per 2,000,000 pounds of soil, gave an annual S increment of 68 pounds.

† Total of 870 pounds, accounted for by 326 pounds from rain water and 544 pounds from  $K_2SO_4$ .

‡ Single incorporation at rate of 2,000 pounds  $CaO$  per 2,000,000 pounds of soil.

§ Single incorporation at rate of 3,750 pounds  $CaO$  per 2,000,000 pounds of soil.

Enhanced outgo, induced by liming treatments	Total outgo	
	Pounds	As per cent of incre- ment†
..	..	79
33	33	83
61	61	86
50	50	84
61	61	86
51	51	84
76	76	87

As per cent of added $K_2SO_4$	Enhanced outgo, induced by liming treatments	
	Pounds	As per cent of incre- ment†
..	..	79
6	33	83
11	61	86
9	50	84
11	61	86
9	51	84
14	76	87

stantially diminished prior to the beginning of the thirteenth year, when the supplemental annual additions of  $K_2SO_4$  were begun. The possibility of losses of sulfur through desulfification has been deemed negligible, because of the inherent oxidative capacity of the soil for additions of elemental sulfur, pyrite, and sphalerite. Any decrease in the sulfur content of a fallow soil is therefore deemed attributable solely to the leaching of sulfates. It appears, therefore, that the greater outgo of sulfates induced by the several liming materials during the final 8-year period was due primarily to the residual effects of the liming materials in accelerating the outgo of moderate incorporations of sulfates, or in diminishing the capacity of the soil to retain the sulfates.

Emphasis should be given to the fact that the data of table 7 were obtained by the use of the silty clay loam after its depletion by cultural cropping, whereas the data of the first six tables relate to an unusual outgo of nutrients from a similar soil of high fertility resultant from an extended period in sod.

#### *Application of the findings as to sulfates*

The results indicate that the ordinary incorporations of fertilizer sulfates will not accomplish a material build-up of the sulfur content of fallow soils. To effect such a build-up, it would seem necessary that the soil be supplied with continuous additions of substantial quantities of sulfates, as supplemental to appreciable increments of rain water and atmospheric sulfates. Such increments decrease in areas remote from urban and coal-consuming centers. Moreover, the possibility of a build-up of sulfate supplies in sandy types of soil would also be much less than in the case of the heavier type of silty clay loam used in the present study. The leaching of sulfates from light sandy soils of low organic matter content would undoubtedly be more rapid and more extensive than that shown for the heavier soils of the present study, and exchange reactions would be less extensive.

In cropped soils, the proportions of rain water leached would be decreased, and the uptake of sulfates by the growing plant would also diminish the amounts of sulfates that would otherwise go out in the leachings. Some of the sulfates used by the plants would also be returned to the soils by root residues. In some localities, rain water sulfur may be appreciable, but it is probable that primary dependence for the conservation of supplies of sulfur must rest upon organic reserves.

It is also apparent that the leachings of sulfates from ordinary additions of calcium and magnesium sulfates will be substantially in the form applied, although some interchange is induced by the cation of the added sulfate, in the absence of liming supplements. The calcium sulfate additions did cause a 27-pound per annum depletion in the magnesium content of the soil; but, this effect was nullified by supplements of high-calcic limestone. The magnesium sulfate additions caused a 78-pound calcium replacement per annum. Neither calcium sulfate nor magnesium sulfate was capable of increasing the outgo of potassium.

The continued additions of potassium sulfate enhanced the quantities of both calcium and magnesium in the free soil-water. Such enhancements were, however, only fractions of the potential exchange capacities of the additions, the larger part of the added potassium sulfate being leached in that form.

#### SUMMARY

A 7-year lysimeter study was conducted with a fertile brown silty clay loam to determine the fate of equivalent annual additions of  $\text{SO}_4$  in combinations with Ca, Mg, and K, and interchange between those cations, with and without single initial supplements of limestone and of dolomite.

Sulfate recoveries of 93 to 100 per cent were obtained, with complete recoveries only from the additions of magnesium and potassium sulfates with dolomitic supplements. Neither limestone nor dolomite caused decreases in  $\text{SO}_4$  outgo.

The maximal outgo of calcium from the unsupplemented sulfates was from the calcium sulfate, about two-thirds of the aggregate addition being recovered. Some increase in calcium outgo was induced by magnesium sulfate and also by potassium sulfate at two rates. The four limestone supplements caused increases of about 150 pounds of  $\text{CaCO}_3$  in annual outgo; the four dolomite supplements induced either meager enhancements or none.

The largest outgo of magnesium from the unlimed units was about 60 per cent of the additions as magnesium sulfate, with small increases attributable to the sulfates of calcium and potassium. A uniform increase of about 125 pounds of magnesium, in terms of  $\text{CaCO}_3$ , was caused by the supplements of dolomite, whereas the outgo of magnesium from each supplement of limestone was less than the outgo from its unlimed control.

The effects of the sulfates of calcium and magnesium, alone and with supplements of limestone and dolomite, on Ca:Mg ratios were noted.

Neither calcium nor magnesium sulfate caused any increase in outgo of potassium from this soil of unusually high content of exchangeable K, whereas both limestone and dolomite repressed the outgo of that element from soil alone and also from the soil treated with potassium sulfate.

Comparisons of outgo of total bases showed that each sulfate treatment caused a cation build-up.

Each indicated interchange induced by the aggregate of the seven annual additions of sulfates was but a small fraction of the potential exchange capacity of the added sulfate.

Another similar soil, of depleted potassium content, that had been limed 12 years previously was used to determine the residual effect of calcic and magnesian materials upon the conservation of  $\text{SO}_4$  from eight annual additions of potassium sulfate. No recovery was equal to the amount added, but an increase in sulfate outgo was induced by each of six liming treatments.

The findings were considered in their relation to the problem of nutrient sulfur in soils of the humid region.



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# INFLUENCE OF SALTS AND SOIL-WATER RATIO ON pH VALUE OF SOILS

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The influence of salts and of the soil-water ratio on soil reaction has been studied by several workers, notably Crowther (2), Bülmann and Jensen (1), and Pierre (3). The general conclusion is that salts depress the pH value, but the magnitude of this effect has not been studied systematically. The conclusion that a twofold dilution causes an increase of 0.1 in pH, so that a 1:5 ratio will have a pH value about 0.25 higher than that of a 1:2 ratio (2), must be considered with reference to the type of soils studied. As a matter of fact, no such simple relationship has so far been discovered to be universal. When diluted, some soils show a marked increase in pH, and others show hardly any change. A closer study of the literature reveals the need for further elucidation to explain the apparent contradictions and discrepancies in the results.

Since the pH value of soil is due to the surface ionization of the colloidal particles and hydrolysis of the exchangeable base, it is reasonable to suppose that the presence of a salt (common ion) would reduce hydrolysis and result in a lowering of the pH value. On the other hand, since the ionization is confined to the surface, mere dilution in the absence of salts may have no marked effect on the pH value of the suspension as a whole. The object of this paper is to describe the experimental evidence brought forth in support of this contention.

## PREPARATION OF THE SOIL

A black cotton soil of high clay content and base exchange capacity was made unsaturated with respect to bases by exhaustive leaching with 0.05 *N* HCl until free from exchangeable Ca, followed by leaching with distilled water until free from Cl ions. The acid-treated soil was neutralized with different bases, so that soils with increasing pH values containing known amounts of exchangeable bases were obtained. The effect of salts and soil-water ratio was studied on these soils. The pH values were determined by the glass electrode using the Cambridge electrometer valve combined potentiometer and pH meter.

## EFFECT OF SOIL-WATER RATIO

The results of the study of the effect of soil-water ratio, given in table 1, show that the same pH is obtained for a given soil even when the soil-water

ratio is varied from 1:5 to 1:25. Erratic values occur here and there, but they do not in any way affect the general conclusion that even a fivefold dilution has virtually no effect on soil reaction. It is noteworthy that other workers have found that the effect of soil-water ratio is greatly reduced in

TABLE 1  
*Effect of soil-water ratio on pH of single-base soils*

SOIL-WATER RATIO	1	2	3	4	5	6
<i>pH values of Na-soil</i>						
1:5	5.70	8.44	9.18	9.94	10.36	....
1:6	5.64	8.42	9.16	9.83	10.38	....
1:7	5.63	8.43	9.14	9.75	10.34	....
1:8	5.63	8.42	9.16	9.76	10.38	.. .
1:10	5.63	8.43	9.22	9.79	10.38	...
1:12	5.63	8.40	9.16	9.82	10.38	...
1:14	5.63	8.71	9.11	9.80	10.40	.. .
1:19	5.66	8.48	9.19	9.85	10.39	....
1:25	5.81	8.48	9.18	9.87	10.38	.. .
<i>pH values of K-soil</i>						
1:5	4.80	6.06	7.40	8.81	9.29	9.86
1:6	4.50	5.68	7.28	8.70	9.44	9.88
1:7	4.50	5.69	7.08	8.72	9.44	9.86
1:8	4.50	5.66	7.10	8.67	9.48	9.87
1:10	4.50	5.69	7.13	....	9.41	9.90
1:12	4.50	5.71	7.28	....	9.48	9.90
1:14	4.58	5.69	7.15	....	9.50	9.94
1:19	4.58	5.71	7.37	8.56	9.50	10.00
1:25	4.80	5.70	7.68	8.86	9.56	9.98
<i>pH values of Ca-soil</i>						
1:5	4.62	5.26	5.64	6.25	7.10	8.75
1:6	4.59	5.22	5.60	6.24	7.14	8.73
1:7	4.53	5.23	5.62	6.26	7.13	8.62
1:8	4.53	5.20	5.60	6.26	7.11	8.62
1:10	4.64	5.27	5.62	6.28	7.12	8.59
1:12	4.70	5.23	5.61	6.29	7.14	8.69
1:14	4.85	5.24	5.64	6.26	7.18	8.60
1:19	4.82	5.21	5.64	6.34	7.11	8.56
1:25	4.86	5.30	5.62	6.33	7.16	8.58

magnitude when the soil is leached with water and redispersed after most of the soluble salts have been removed (1). The results with soils neutralized to higher pH values are of interest, because in these soils a certain amount of hydrolysis might be expected as a result of dilution, but even in these soils the effect of dilution is not noticeable. Apparently the pH value is governed

entirely by the nature and amount of exchangeable base, and no appreciable quantity of metallic hydroxide is present even at pH 10 in these mixtures.

#### EFFECT OF SALTS

The effect of salts was studied by using chlorides of various ions, the corresponding metallic chloride being used for every exchangeable base. Ten-gram portions of soils at different pH values were suspended in 50 cc. of water, and normal solutions of the corresponding chlorides were added in 1-cc. lots up to 50 cc. The addition of these solutions undoubtedly caused some dilution of the suspension, but as we have seen that dilution alone has no effect on pH, this was ignored. It was also ascertained by direct experiment that results are substantially the same when increasing quantities of salts in the solid state are added.

The results for Na, K, and Ca are given in table 2, and those for Mg, Ba, Sr, and Li are plotted in figure 1. All the curves obtained are similar, and, therefore, only a few are given by way of illustration. An initial rapid fall is followed by a more gradual one. The initial fall is greater in the acid range and becomes less when the pH is high. When the curves are plotted on a semilogarithmic scale; that is, pH values against log concentration of salt, we get a series of parallel straight lines, the slope of which is characteristic of the basic radical. The following relations are found to hold for various soils:

$$\text{pH} = \text{pH}_0 - K \log C$$

where pH is the initial pH without any salt;  $C$  is the concentration of the salt in milliequivalents per 100 gm. of soil; and  $K$  is a constant, characteristic of the basic ion.

The values of  $K$  for various ions are as follows: Li = 0.30, Na = 0.79, K = 0.55, Ca = 0.48, Mg = 0.48, Ba = 0.26, Sr = 0.28.

It is to be remembered that the effect of salts in lowering the pH values of soils is analogous to a similar effect in ordinary buffer solution. Thus it can be shown that the pH value of sodium carbonate-bicarbonate mixture is less in the presence of KCl than in its absence (4).

A closer study of these results presents some interesting aspects which would offer a rational explanation of the discrepancies observed by previous workers in the effect of soil-water ratio on pH values. It is clear that in the steeper portion of the curve a very small concentration of salts such as would be ordinarily found in most of the normal soils would materially alter the pH value. Since this effect does not depend on the absolute quantity of the salt, but rather on its concentration in a suspension, dilution will have the effect of raising the pH value, and the magnitude of this change will be governed entirely by the nature and quantity of the salt present in the soil. These results also lead to the conclusion that measurement of the pH values of soils in  $N$  KCl solution would give more reproducible results in the hands of different workers, for not only would the effect of soil-water ratio be negligible,

TABLE 2  
*Effect of salts on pH value of single-base soils*

CC. OF N SOLUTION ADDED TO 50 CC. OF SUSPENSION	1	2	3	4	5	6	7
<i>NaCl added to Na-soil</i>							
0	5.69	6.84	8.44	9.43	10.00	10.37	....
1	5.63	5.91	7.68	9.90	9.52	10.10	....
2	5.38	5.62	7.49	8.79	9.38	10.00	....
3	5.22	5.46	7.32	8.64	9.30	9.94	...
4	4.13	5.34	7.22	8.57	9.22	9.86	....
5	4.05	5.23	7.15	8.53	9.18	9.83	....
6	3.94	5.18	7.10	8.46	9.12	9.80	....
7	3.91	5.11	7.00	8.41	9.11	9.78	...
8	3.86	5.08	6.95	8.36	9.09	9.70	....
9	3.82	4.99	6.88	8.29	9.02	9.71	...
10	3.82	4.98	6.84	8.24	9.00	9.68	....
15	3.72	4.88	6.77	8.16	8.92	9.60	....
20	3.64	4.80	6.66	8.08	8.85	9.53	....
25	3.60	4.74	6.65	8.02	8.78	9.52	....
30	3.57	4.70	6.58	8.00	8.75	9.44	....
35	3.56	4.66	6.54	7.93	8.73	9.41	...
40	3.56	4.66	6.50	7.92	8.65	9.37	...
50	3.55	4.62	6.48	7.86	8.59	9.34	...
Total change. ...	2.14	2.22	1.96	1.57	1.41	1.03	....
<i>CaCl<sub>2</sub> added to Ca-soil</i>							
0	4.48	4.95	5.96	7.36	7.94	8.26	8.59
1	3.34	3.80	4.73	6.74	7.14	7.72	7.88
2	3.23	3.71	4.51	6.56	6.95	7.55	7.68
3	3.22	3.60	4.44	6.47	6.86	7.49	7.64
4	3.16	3.56	4.32	6.40	6.89	7.44	7.55
5	3.15	3.50	4.30	6.38	6.90	7.40	7.54
6	3.13	3.49	4.26	6.33	6.90	7.36	7.49
7	3.12	3.51	4.24	6.25	6.85	7.33	7.46
8	3.10	3.49	4.20	6.25	6.82	7.32	7.41
9	3.08	3.49	4.20	6.22	6.78	7.30	7.38
10	3.13	3.49	4.18	6.24	6.76	7.27	7.38
15	3.10	3.44	4.14	6.12	6.68	7.21	7.30
20	3.08	3.42	4.13	6.08	6.62	7.16	7.30
25	3.08	3.44	4.10	6.08	6.58	7.15	7.25
30	3.14	3.43	4.08	6.00	6.50	7.14	7.29
35	3.14	3.43	4.08	6.00	6.50	7.06	7.20
40	3.16	3.43	4.08	5.97	6.50	7.02	7.18
50	3.16	3.41	4.08	5.93	6.46	7.04	7.16
Total change. ....	1.32	1.54	1.88	1.43	1.48	1.22	1.43

TABLE 2—*Concluded*

CC. OF N SOLUTION ADDED TO 50 CC. OF SUSPENSION	1	2	3	4	5	6	7
<i>KCl added to K-soil</i>							
0	5.09	5.98	7.40	8.90	9.35	10.02	....
1	4.31	5.47	7.06	8.38	9.04	9.81	....
2	4.04	5.29	6.92	8.26	8.91	9.74	....
3	3.83	5.16	6.82	8.08	8.87	9.65	....
4	3.74	5.06	6.70	7.94	8.82	9.62	....
5	3.64	4.96	6.64	7.78	8.73	9.52	....
6	3.60	4.86	6.62	7.78	8.72	9.50	....
7	3.55	4.82	6.62	7.78	8.63	9.48	....
8	3.51	4.76	6.54	7.70	8.61	9.48	....
9	3.46	4.73	6.48	7.67	8.57	9.42	....
10	3.46	4.70	6.42	7.61	8.54	9.40	....
15	3.46	4.62	6.41	7.51	8.47	9.34	....
20	3.41	4.55	6.37	7.46	8.42	9.24	....
25	3.42	4.53	6.32	7.42	8.35	9.19	....
30	3.42	4.49	6.30	7.38	8.29	9.17	....
35	3.42	4.45	6.28	7.35	8.27	9.16	....
40	3.42	4.42	6.20	7.30	8.25	9.12	....
50	3.42	4.38	6.18	7.27	8.23	9.12	....
Total .. . . .	1.67	1.60	1.22	1.63	1.12	0.90	....

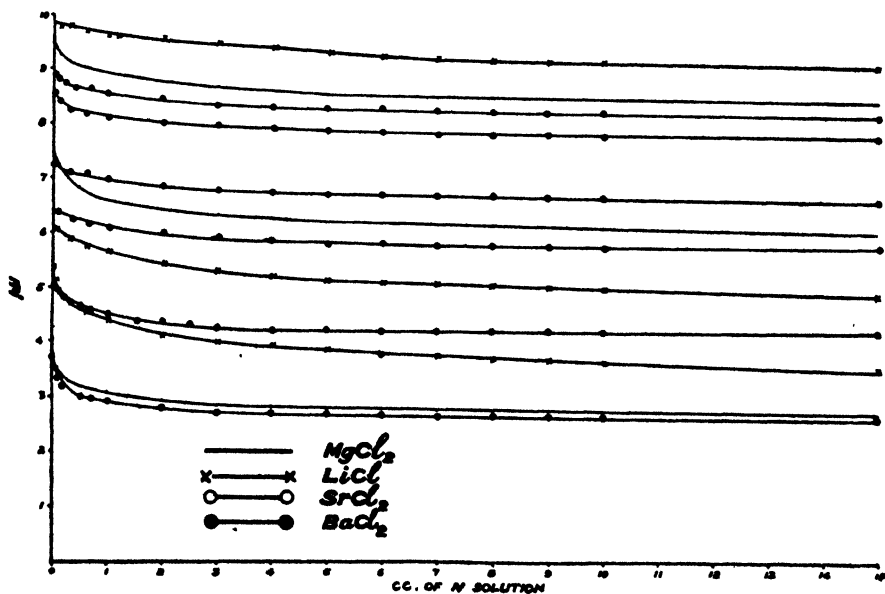


FIG. 1. EFFECT OF MAGNESIUM, LITHIUM, STRONTIUM, AND BARIUM CHLORIDES ON THE pH VALUES OF THEIR CORRESPONDING SOILS



but day by day variations in natural soils which are obviously due to changes in salt content would disappear and the pH value of a soil would assume the importance of a fundamental constant. In order to determine whether the general conclusions reached for this soil are applicable to other soils, 10 soils were taken. These soils were first made unsaturated by 0.05 *N* HCl treatment and then brought to a pH between 6 and 7 by the addition of KOH. The effect of increasing amounts of KCl was studied on these soils. The results when plotted on a semilogarithmic scale, i.e., pH against log concentration, give a series of parallel lines. In table 3 are given the pH values of the K-soils both in water and in *N* KCl. The difference, in general, is of the order of 2.

Since the presence of salts depresses the pH value of soil, leaching should result in a rise in the pH value. This has been noticed by other workers. To study the effect in greater detail, 20 soils were leached first with water

TABLE 3  
*The pH values of K-soils at two different pH levels in water and in N KCl*

SOIL NUMBER	pH			pH		
	In water	In <i>N</i> KCL	Difference	In water	In <i>N</i> KCL	Difference
M1.....	8.34	6.36	1.98	6.00	3.88	2.12
M2.....	8.23	6.14	2.09	6.35	4.48	1.87
M5.....	7.23	5.54	1.69	5.84	4.00	1.84
M6.....	7.40	5.31	2.09	5.50	3.64	1.86
M9.....	7.98	6.13	1.85	6.43	4.53	1.90
M12.....	7.63	5.85	1.78	5.86	3.90	1.96
M15.....	9.14	6.99	2.15	....	....	....
M23.....	8.27	6.18	2.09	....	....	....
P.C. 7.....	6.92	4.56	2.36	....	....	....
P.C. 15....	6.24	4.58	1.66	....	....	....

then with alcohol, and dried. The purpose of the final leaching with alcohol was to facilitate drying and removal from the filter paper. The washed soils were suspended in water, and the pH values were determined in the usual way, both in water and in *N* KCl. The pH values of the original soils in water and in *N* KCl were also determined. The results are given in table 4, from which the following conclusions may be drawn:

The pH value of the leached soil is always higher than that of the unleached soil.

This difference becomes inappreciable when pH is determined in *N* KCl.

The effect of KCl in lowering the pH value is greater in the leached than in the original soil.

The difference between the change in pH value due to KCl in the leached and in the unleached soil is of the same order as the rise in pH value of the original soil due to leaching.

It will be seen that the discrepancies in the literature regarding the effect of soil-water ratio on reaction are satisfactorily explained by the fact that

salts lower the pH value of soils. The fact that soil reaction shows rapid fluctuations can also be understood, since it is associated with changes in the salt content of the soil. It is also clear that the pH value determined in *N* KCl will not be subject to rapid changes, and such a value could be used as a fundamental constant for the soil. The pH values in *N* KCl are easily determined both colorimetrically and electrometrically and will show much greater consistency in the hands of different workers than will pH values

TABLE 4  
*Effect of washing and of KCl on soil reaction*

SOIL NUMBER	CLAY	pH VALUES*							
		W	WK	d	U	UK	d'	(W-U)	(d-d')
	<i>per cent</i>								
P.C. 1 .	11.3	8.86	8.07	0.79	8.07	7.90	0.17	0.79	0.62
P.C. 2 .....	59.3	9.18	7.24	1.94	8.24	7.12	1.12	0.94	0.82
P.C. 3 .....	62.2	7.72	6.18	1.54	7.61	6.34	1.27	0.11	0.27
P.C. 4 .....	15.2	8.89	7.37	1.52	8.16	7.74	0.42	0.73	1.10
P.C. 5 .....	12.3	8.89	8.00	0.89	8.34	7.84	0.50	0.55	0.39
P.C. 6 .....	28.4	5.99	4.31	1.68	5.18	4.18	1.00	0.81	0.68
P.C. 7 .....	21.8	9.86	8.38	1.48	9.50	8.62	0.88	0.36	0.60
P.C. 8 .....	25.2	8.66	7.46	1.20	8.28	7.40	0.88	0.38	0.32
P.C. 9 .....	21.6	6.66	5.09	1.57	5.70	4.83	0.87	0.96	0.70
P.C. 10 . . .	35.6	9.11	7.43	1.68	8.54	7.50	1.04	0.57	0.64
P.C. 11 .....	32.8	8.86	7.42	1.44	8.40	7.36	1.04	0.46	0.40
P.C. 12 .....	7.2	6.43	4.88	1.55	5.24	4.58	0.66	1.19	0.89
P.C. 13. ....	58.9	8.79	7.27	1.52	8.32	6.96	1.36	0.47	0.16
P.C. 14.....	21.5	6.14	4.66	1.48	5.48	4.52	0.96	0.66	0.52
P.C. 15.....	22.4	8.47	7.71	0.76	7.66	7.58	0.08	0.81	0.68
P.C. 16 .....	8.7	8.88	8.17	0.71	8.39	8.08	0.31	0.49	0.40
P.C. 17.....	14.1	8.64	7.66	0.98	7.82	7.58	0.24	0.82	0.74
P.C. 19.....	42.3	8.77	7.44	1.33	8.14	7.24	0.90	0.63	0.43
P.C. 21.....	13.5	9.12	7.38	1.74	8.17	7.45	0.72	0.95	1.02

- \* W = pH value of washed soil in water.
- WK = pH value of washed soil in *N* KCl.
- U = pH value of original soil in water.
- UK = pH value of original soil in *N* KCl.
- d = W - WK.
- d' = U - UK.

in water. The effect of soil-water ratio is also inappreciable when pH values are determined in *N* KCl. This will be seen from table 5.

Some difficulty undoubtedly will be experienced in the interpretation of results by those who are used to determining pH values in water suspensions; but this difficulty will disappear when it is remembered that the pH values of washed soil in *N* KCl solution are in the majority of cases lower by approximately 1.5 than those in water suspension. This fact would be found helpful

for the mental adjustment in the initial stages. It may even be desirable to determine the pH value both in water and in *N* KCl for some time as is the custom in certain soil laboratories, but it must be remembered that whereas the pH in water is partly arbitrary and likely to fluctuate from day to day, the pH value in *N* KCl is more closely related to the state of saturation of the exchange complex in the soil, which will not change in comparatively short intervals of time. Many workers prefer the use of *N* KCl for determining soil reaction, and the present work offers a rational explanation for this preference.

TABLE 5

*Effect of soil-water ratio on the reaction of noncalcareous soils in water and in N KCl*

SOIL-WATER RATIO	P.C. 3		P.C. 4		P.C. 6		P.C. 8		P.C. 9		P.C. 10	
	KCL	Water	KCL	Water	KCL	Water	KCL	Water	KCL	Water	KCL	Water
1:2.5	6.18	7.57	7.62	8.26	4.20	5.35	7.14	8.42	4.86	5.85	7.22	8.48
1:5	6.22	9.83	7.62	8.42	4.26	5.55	7.14	8.66	4.86	5.99	7.20	8.78
1:7	6.22	7.95	7.62	8.42	4.30	5.58	7.19	8.72	4.88	6.02	7.19	8.82
1:8	6.24	8.06	7.62	8.45	4.32	5.58	7.21	8.72	4.90	6.08	7.20	8.86
1:10	6.25	8.16	7.62	8.52	4.33	5.60	7.22	8.76	4.90	6.08	7.32	8.96
1:12	6.26	8.26	7.63	8.51	4.34	5.64	7.14	8.76	4.93	6.11	7.42	9.01
1:14	6.25	8.26	7.63	8.52	4.39	5.61	7.22	8.76	4.92	6.14	7.42	9.05
1:19	6.14	8.46	7.63	8.56	4.39	5.71	7.21	8.80	4.92	6.17	7.42	9.11
1:25	6.18	8.46	7.55	8.58	4.42	5.79	7.05	8.80	4.93	6.23	7.40	9.21

TABLE 6

*Effect of soil-water ratio on the reaction of calcareous soils in N KCl*

SOIL-WATER RATIO	NON-CALCAREOUS SOILS PLUS $\text{CaCO}_3$						NATURALLY CALCAREOUS SOILS			
	P.C. 3	P.C. 4	P.C. 6	P.C. 8	P.C. 9	P.C. 10	1	2	5	7
1:2.5	6.62	7.62	7.62	6.76	6.92	7.27	7.9	6.95	7.80	8.60
1:5	6.63	7.73	6.84	6.84	7.03	7.43	8.12	7.10	7.94	8.80
1:7	6.72	7.84	7.05	7.84	7.06	7.53	8.22	7.18	8.13	8.92
1:8	6.79	8.00	7.18	7.88	7.22	7.64	8.39	7.32	8.25	8.99
1:10	6.90	8.03	7.22	7.97	7.32	7.76	8.48	7.42	8.34	9.04
1:12	6.97	8.17	7.25	8.00	7.41	7.89	8.53	7.42	8.42	9.10
1:14	7.00	8.23	7.28	8.05	7.53	7.94	8.64	7.54	8.49	9.16
1:19	7.08	8.31	7.30	8.13	7.61	8.02	8.79	7.61	8.55	9.24
1:25	7.17	8.67	7.41	8.72	7.75	8.18	8.86	7.71	8.68	9.32

#### RÔLE OF $\text{CaCO}_3$ IN SOIL REACTION

The effect of a slightly soluble substance like  $\text{CaCO}_3$  on soil reaction needs special attention. It is conceivable that even in the absence of other salts,  $\text{CaCO}_3$  would modify the soil reaction, even in the presence of *N* KCl. This was actually observed both in natural calcium soils and in soils to which  $\text{CaCO}_3$  was added and which without  $\text{CaCO}_3$  had shown no effect of soil-water ratio

in *N* KCl (table 5). The results given in table 6 show that the effect of soil-water ratio persists even in *N* KCl on soils containing  $\text{CaCO}_3$ . For such soils, therefore, the soil-water ratio will still have to be defined even when pH values are determined in *N* KCl.

#### SUMMARY

The effect of salts and soil-water ratio on soil reaction has been studied.

The salts have a profound influence on soil reaction, which alters appreciably in the presence of even small quantities of neutral salts.

The effect of soil-water ratio on soil reaction is indirect insofar as the soil-water alters the concentration of salts present.

In the absence of salts, the pH value is not affected by soil-water ratio.

Since natural soils contain varying amounts of salts, uniformity of results can only be obtained by determining soil reaction in *N* KCl solution.

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# A THEORY EXPLAINING THE RELATION OF SOIL-WATER RATIOS TO pH VALUES<sup>1</sup>

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In the determination of soil reaction or pH values, the use of a highly artificial condition which never exists in the field is a commonly accepted practice. High dilutions of soil to water are used because of the type of apparatus which is employed for hydrogen-ion determinations and because of the fact that only at high ratios of soil to water are constant values for the same soil obtained. The exact ratio of soil to water employed varies with the different investigators. The literature on the ratio and the effect of dilution is voluminous, but there is actually little correlation among the results of the different investigators. Some report an increase in acidity with dilution, others find an increase in alkalinity, and still others find no change in pH. The general trend, as shown by the referee report of McGeorge (5), is toward an increase in pH with dilution.

With the introduction of the glass electrode and its subsequent development, hydrogen-ion determinations may now be made at a much lower ratio of soil to water. Using a colorimetric method, Wilcox (10) measured the pH of the displaced solution at soil moisture-holding capacity. Heintze (1) was able to determine the pH of soils at their sticky point, but because of the type of glass electrode used, he was unable to get a good contact between the soil and electrode at a lower moisture content. McGeorge (4), with the use of the Beckman Spear-Type glass electrode, has shown that it is possible to obtain the pH values of semiarid soils with as low a moisture content as 6 per cent. It now appears probable that the soil reaction may be ascertained under field moisture conditions instead of under the highly artificial state established in the laboratory. In this study, the reaction of representative soil types of the State of Washington was determined at the normal field moisture content and compared with the values at higher dilutions of soil to water.

## PROCEDURE AND RESULTS

A moisture content approximating that of the normal moisture percentage of the soils used was obtained by carefully tamping air-dried soil passed

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through a 2 mm. sieve in 100 cc. graduate cylinders, and adding  $\text{CO}_2$ -free distilled water in small increments until approximately 2 inches of dry soil remained in the bottom of the cylinder. The cylinders were then tightly stoppered and allowed to stand undisturbed for 48 hours until approximate moisture equilibrium conditions were established. In a later study it was found that although a period of 36 hours was sufficient for complete penetration of the water in all soil types, a slow distribution continued, so that the moisture content obtained even at 48 hours, especially in the heavier soils, was slightly higher than the normal moisture percentage.

The hydrogen-ion concentration was determined by transferring the moist soil to a small beaker and gently pressing it around a special calomel type glass electrode made by the author. The electrode, as described by Peech (7), consisted of a saturated calomel electrode inserted in a short length of 0.015 Corning glass, which had a thin bulb blown at one end. Contact was made by means of a mercury connection, the whole electrode being a single complete unit when assembled. The moisture content of the soil was determined immediately after the pH values were determined. Values of the hydrogen-ion concentration of the same soils were determined in soil-water ratios of 1:10, 1:5, and 1:1,  $\text{CO}_2$ -free distilled water being used in all soil suspensions. The resulting values for the representative soils are given in table 1.

The condition under which the soil reaction is determined evidently has a great influence on the magnitude of the pH value obtained. As the soil-water ratio narrows to 1:1, the pH value of the soil decreases. This is in accordance with the findings of other investigators (3, 5, 8, 9) and may be explained by the increase in hydroxyl ions on dilution. The Debye and Hückel activity theory must also be considered. As the soil-water ratio becomes narrower, the concentration of the ions in the soil suspension will increase with subsequent decrease in ion activity.

When the soil reaction is determined at approximately normal moisture conditions, the decrease in pH values with decreasing moisture content is no longer continued in all soils. The decrease continues only in those soils which are approximately neutral, but in the more acid soils the pH values increase at approximately normal field conditions as compared to a 1:1 ratio of soil to water. In several of these acid soils the resulting values at the normal moisture percentage are higher than those obtained at a 1:5 ratio, and in a few exceptional soils they are higher than those at a 1:10 ratio. Wilcox (10) also found an irregular change in pH values with soil-water ratios in different soils. In four of the six soils listed by him, the pH values increased at the moisture-holding capacity as compared to higher dilutions.

Before any explanation of this phenomenon was attempted, it was thought advisable to determine whether this change in pH was observable in soils representing different extreme types. The values for these different soils are given in table 2. When an excess of water is present in these soils, as in

those previously examined, a decrease in the pH values occurs with a decrease in the soil-water ratio. At approximately normal moisture percentage the values of the alkaline and neutral soils continue to decrease, whereas those of the acid soils increase or decrease as compared to a 1:1 ratio of soil to water.

TABLE 1

*pH values at different soil-water ratios of representative soil series in the State of Washington*

SOIL NUMBER	SOIL SERIES	RATIO 1:10	RATIO 1:5	RATIO 1:1	NORMAL MOISTURE	NORMAL MOISTURE
		pH	pH	pH	pH	per cent
1	Hesson	5.50	5.31	5.24	5.47	46.46
2	Felida	6.24	5.93	5.74	5.92	32.20
3	Everett	5.71	5.77	5.38	5.88	32.99
4	Puget	5.77	5.54	5.35	5.51	35.75
5	Chehalis	5.68	5.48	5.19	5.25	70.95
6	Melbourne	5.08	4.92	4.68	5.34	59.10
7	Salkum	5.72	5.49	5.46	5.60	33.21
8	Olympic	5.66	5.56	5.25	5.69	54.29
9	Walla Walla	6.25	6.32	5.86	5.32	25.81
10	Hoquiam	5.06	4.95	4.81	5.31	52.53
11	Spanaway	5.78	5.71	5.43	5.99	24.78
12	Garrison	7.22	7.14	6.80	6.25	29.27
13	Ephrata	7.30	7.00	7.02	6.82	24.00
14	Cashmere	6.98	6.98	6.68	6.91	17.65
15	Palouse	6.81	6.60	6.33	6.03	26.73
16	Ritzville	6.19	5.97	5.56	5.71	30.11
17	Lynden	5.74	5.83	5.56	5.77	18.37

TABLE 2

*pH values at different soil-water ratios*

SOIL NUMBER	SOIL	RATIO 1:10	RATIO 1:5	RATIO 1:1	NORMAL MOISTURE	NORMAL MOISTURE
		pH	pH	pH	pH	per cent
18	Alderwood (Washington)	5.17	4.92	4.82	5.34	30.06
19	Podzolic (Washington)	5.64	5.83	5.65	5.48	26.94
20	Mohave (Arizona)	8.35	8.42	7.96	6.71	18.13
21	Lakewood (New Jersey)	4.74	4.56	4.04	4.05	24.50
22	Greenville (Florida)	5.75	5.70	5.39	5.19	20.66
23	Houston (Texas)	8.32	8.08	7.51	6.58	54.02
24	Barnes (North Dakota)	7.64	7.44	7.07	6.82	47.17
25	Black Alkali (Washington)	10.17	10.04	9.82	8.40	35.69

Mattson (6) has shown that the exchangeable ions in the colloidal micelle have varying degrees of dissociation, depending on their hydration and electrostatic forces. Their order of dissociation, in general, follows the Hofmeister series. When the soil-water ratio is such that free water is present, the exchangeable ions have a high degree of dissociation. At approximately



normal moisture percentage, insufficient water is present to allow as high a degree of dissociation of the exchangeable cations; therefore, preferential dissociation results, in which those ions which dissociate most readily dissociate to the greatest degree. Thus there will be a preferential dissociation of the metallic cations over the hydrogen ions. As the pH of the soil suspension is dependent upon the concentration and type of ions dissociating from the colloidal micelle, the pH value of the soil suspension will be higher in the case of preferential dissociation than in the case of complete dissociation. Jarusov (2) has shown, however, that certain factors such as organic matter, degree of saturation, and kinds of exchangeable cations influence the mobility of the exchangeable cations in the soils. For this reason, in certain soils hydrogen may be more mobile than the metallic cations, with the result that preferential dissociation will cause a lower pH value instead of a higher.

Another influence on the pH values of the soil suspension is the Debye Hückel activity effect, which is a function of the valence and concentration of the ions in the soil suspension. Thus both preferential dissociation and the Debye Hückel activity effect may serve as a basis for explaining the difference in pH value occurring at the normal moisture content as compared to the 1:1 ratio of soil to water. In the alkaline and neutral soils the concentration of the metallic cations is such that the Debye Hückel activity effect will overshadow any effect of preferential dissociation of the metallic cations over hydrogen. In the acid soils that exhibit an increase in the pH values, the preferential dissociation of the metallic cations over hydrogen predominates. The few acid soils that show a continued decrease in the pH values may be the result of a condition in which the hydrogen is more mobile than the metallic cations.

In order to substantiate the theory, two soils were prepared in which only two different types of cations, hydrogen and calcium, or hydrogen and sodium, were present in the micelle. If the theory of preferential dissociation is valid, there should be a ratio of the metallic cations to the hydrogen ions at some low moisture range at which, because of the effect of preferential dissociation, an increase in pH would result upon a further decrease in the moisture content.

A soil was completely desaturated by leaching with 0.05 *N* HCl; its total base-exchange capacity was determined with ammonium acetate; and different portions were saturated to different degrees with Ca or Na by the addition of the proper amounts of calcium or sodium hydroxide. The reaction of these variously saturated soils was determined at different soil-water ratios and at approximately normal moisture percentage. The data are recorded in table 3, in which the same phenomenon is demonstrated as was exhibited in the natural soils. Below 50 per cent base saturation, there is an increase in the pH values at normal moisture percentage as compared to a soil-water ratio of 1:1.

Both the artificially prepared soils and the soils in their natural condition substantiate the theory of preferential dissociation. In general, the acid

soils increase in pH values as a result of a decrease in the moisture content of the soil from a 1:1 ratio to normal moisture capacity, indicating a dominance of preferential dissociation. The pH values of the alkaline and neutral soils continue to decrease, showing that in these soils the "activity effect" is greater than the effect of preferential dissociation.

At approximately normal moisture percentage, as compared with higher moisture contents, the increase in pH in the podzol and lateritic soils is negligible, as would be expected from the theory of preferential dissociation. Since these soils are nearly completely desaturated, the hydrogen ions dominate in the micelle and soil suspension. Thus, both the effect of preferential dissociation and the Debye Hückel activity effect will be opposite, small, and nearly equal. This is shown in the values obtained for these two soils. A slight reduction in the pH values takes place in the lateritic soil; in the pod-

TABLE 3  
*Effect of percentage base saturation on pH values at different soil-water ratios*

TREATMENT	RATIO 1:10	RATIO 1:5	RATIO 1:1	NORMAL MOISTURE
	pH	pH	pH	pH
100 per cent Ca saturation	6.90	6.85	5.73	5.68
75 per cent Ca saturation	6.27	6.27	5.38	4.98
50 per cent Ca saturation	5.18	5.13	4.36	4.25
25 per cent Ca saturation	4.42	4.17	4.02	4.12
10 per cent Ca saturation	4.43	4.05	3.86	3.94
0 per cent Ca saturation	3.75	3.77	3.75	3.89
100 per cent Na saturation	7.10	6.98	6.00	6.10
75 per cent Na saturation	6.83	6.70	5.94	5.89
50 per cent Na saturation	5.76	5.59	4.86	4.91
25 per cent Na saturation	5.37	5.10	4.42	4.52
10 per cent Na saturation	4.76	4.45	4.00	4.27
0 per cent Na saturation	4.00	3.75	3.80	3.89

zol a neutralization of the two factors occurs, with the pH value remaining constant.

In a soil which exhibits the influence of the counteraction of the Debye Hückel activity effect and the effect of preferential dissociation, there should be a soil-water ratio at which the pH value is at a minimum. At this ratio the amount of water present in the soil suspension would be just sufficient for a high dissociation and concentration of the cations in the micellar solution. This point should lie just below the maximum water-holding capacity of the soil. Several soils were selected to determine whether this point of minimum pH value could be attained. The total pore space was calculated from the volume weight of the respective soils. Sufficient water was added to bring them just to saturation. The reactions were measured, and the results, recorded in table 4, indicate that the pH value obtained at the point of saturation is lower than that for any other soil-water ratio of these respective soils.

The theory of preferential dissociation explains the increased pH values of certain soils at approximately normal moisture percentage as compared to those at higher soil-water ratios. The data from the artificially prepared soils and the minimum pH values obtained at moisture saturation strongly support the theoretical considerations. As the counteraction between the "activity effect" and preferential dissociation due to changes in moisture content will be a factor in the seasonal fluctuations in the pH of soils under natural field conditions, the pH value of the soil obtained at the normal moisture content is more representative of the soil reaction under field conditions and appears to give a truer picture of the actual conditions under which plants grow than the values obtained under the highly artificial conditions now employed.

TABLE 4  
*Soil-water ratios showing a point of minimum pH*

SOIL NUMBER	RATIO 1:10	RATIO 1:5	RATIO 1:1	SATURATION	NORMAL MOISTURE
	pH	pH	pH	pH	pH
3	5.71	5.77	5.38	5.19	5.88
6	5.08	4.92	4.68	4.37	5.34
11	5.78	5.71	5.43	5.36	5.99
18	5.17	4.92	4.82	4.65	5.34

#### SUMMARY

The determination of the pH values of several soils at different soil-water ratios, ranging from a ratio of 1:10 to approximately normal moisture capacity, shows that the condition under which the soil reaction is determined by the use of a glass electrode has a pronounced influence on the pH value obtained.

In acid soils the minimum pH value occurs when the soil-water ratio is at the point of the water-holding capacity of the soil. A further reduction in the soil moisture content results in increased pH values because the proportion of metallic cations to hydrogen ions is low enough to produce a counteraction of the Debye Hückel activity effect by the effect of preferential dissociation.

In the more alkaline soils, the proportion of metallic cations is much higher than that in acid soils; therefore, the "activity effect" overshadows the effect of preferential dissociation, with the result that a continued decrease in pH values takes place with decreasing moisture content.

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## ON THE FORMATION OF STRUCTURE IN SOIL: V. GRANULAR STRUCTURE

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The prevailing conception of structure formation in soil tends to limit this process to a definite range of phenomena and to associate it with the genesis of various soils. Structure thus assumes the character of a general property of soil and the significance of an organizational symptom closely connected with the chemical and physical properties of soil. Questions of morphogenesis are still unexplained, however, and information of but the most general character is available concerning the relation of the form of structural aggregates to the inherent properties of soil. The purpose of this paper is to summarize some results of the author's studies on the origin of structural forms in connection with the alteration of the composition of soil. Although it is not yet possible to explain all the various forms, the theoretical investigation of this problem may have a practical application.

The greatest interest is presented by the durable granular structure possessed mainly by the upper layers of humus-rich soils. The typical granularity of such soils is distinguished by the black color and the considerable solidity and size (3-7 mm.) of the grains (2) and by the shape of the structural aggregates, which manifests itself in the formation of small clods, some of which are spheric, and some of which have irregular, angular surfaces.

Granular structure is altered or destroyed by certain factors. As has been noted, the accumulation of sand in chernozem weakens and destroys the structure, and this action is readily explained by conditions which affect the state of equilibrium (4). In regions of solonetz soil, typical granular structure is transformed into a "cloddy-granular" or even a "prismatic-granular" structure (2), in which the grains become more compact and acquire a pronounced brilliancy and an angular surface. In dry steppe chernozems, the grains become less compact as a result of the insignificant quantity of humus in the soils; their color changes to brown. The size of the grains decreases, and in some places granularity disappears completely, the structure passing into another type—the laminar (2). Loss of typical granularity takes place in the process of podzolization of chernozems. At certain stages of degradation, accompanied by the destruction of a part of the organic matter content, "granularity is still preserved, but the grains lose their compactness and form" (2). With increased decomposition of organic substance, "the clarified mass of the soil, on drying, begins to break up into laminar fragments" (2).

The inverse process of the restitution of structure in those soil layers in which it has been destroyed, is also observed in nature. Thus, "forest-steppe soils, possessing a laminar structure, become granular when their humus content increases as a result of encroachment of steppe vegetation upon forest areas" (2). It is a well-known fact, as well, that pulverized arable soils regain granularity under the influence of perennial meadow vegetation.

Both phenomena—the destruction and the restitution of granular structure—deserve most serious attention and study (2). The explanation of the origin of granular structure and of the processes involved in its destruction may be based on the study of relative states of equilibrium in sand-clay-humus mixtures. Important circumstances which may be of service in the elucidation of these phenomena are as follows:

The appearance of the *spheric* and *laminar* forms is the extreme manifestation of the symptoms of restitution and destruction of granular structure.

In the restitution and destruction of granular structure there is a gradual transition from one form to the other, and this transition is invariably related to the alteration in the content of organic matter.

The sand-clay-humus mixture having an excess humus content is an unstable system. When such a mixture is dried or frozen, it separates into two distinct parts (pl. 1). One of these, the anisotropic, consists of laminar particles of humus-clay-sand. The other is organic matter, which separates from the mixture after clay is "saturated" with humus. The disintegration of the mixture results from the difference in the surface tension of its components. The anisotropic component is a medium of high viscosity and comparatively low surface tension; the organic, isotropic component has the same capillary constant as water. Because of this difference in surface tension, the organic matter must distribute itself at the periphery of the anisotropic substance, which occupies the central position. According to the theory of Curie (1), the capillary constant of isotropic substance is the same in every direction, and this condition corresponds to a *minimum surface or to the spheric form*. Consequently, amorphous organic substance, distributed at the periphery of a structural aggregate, determines the shape of the latter. Such an aggregate must possess a spheric or a nearly spheric form. The inner part of the structural aggregate is a crystalline substance with a minimal surface tension, and it must, therefore, have a flat surface and a polyhedral form. Since the disintegration takes place long before the solidifying of the medium, while the latter is still viscous, the mechanical resistance does not exceed the surface tension, a situation which makes possible the application of the theory of Curie to a system of this kind. At the surface of delimitation—organic substance-air—the superficial rows of micellas of the organic matter are oriented and form a semipermeable layer (4). The formation as a whole, that is, the soil aggregate, is a kind of cell, possessing osmotic properties. The spheric form of granular structure is a sign of the accumulation of an amorphous

layer of humus at the periphery, as a result of which the granular aggregates have an immense surface enclosed in a small volume.

The destruction of granularity must be accompanied by the elimination of the surface layer of amorphous organic matter. As this layer is gradually eliminated, the polyhedral form of the inner anisotropic substance becomes more and more apparent, and the gradual transition to the cloddy-granular or prismatic-granular structure of the weakly solonetz and weakly degraded chernozems occurs. If this process of degradation is intensified, however, and the destruction of this humus layer progresses, the soil mass becomes laminated (3).

Granularity is destroyed also during the plowing and cultivating of soil. The process of destruction is related not only to the direct action of the implement, but also to the resulting change in the normal distribution of the aggregates in the soil layer. Under the influence of the atmosphere, of the changes in the conditions of aeration, of the change of vegetation and micro-organisms, the oriented layer of organic substance at the surface of the aggregate is destroyed. The state of equilibrium of the amorphous layer of humus is unsettled, and the separation into smaller parts takes place. The fact that the rapid rate at which structure is destroyed under the influence of tillage is out of all proportion to the decrease of the supply of humus in soil, bears out this interpretation (2). As has been noted by many investigators, the humus supply, by itself, does not ensure a stable granular structure. A necessary condition for the formation of stable aggregates is *the formation of a metastable envelope of oriented substance at the surface of the amorphous humus layer, which preserves the microaggregate from division* (3, 4).

The process of the restitution of granular structure consists in the formation of a layer of amorphous organic substance around a laminar aggregate. The permeation of the aggregate, already existing in the soil, by organic matter and the accumulation of firmly bound humus are determined by the state of equilibrium of the anisotropic lamina. Beyond this limit there is no binding of humus, and the excess organic matter gathers at the *periphery* of the lamina, transforming it into a granular aggregate. It is to be presumed, therefore, that the formation of grains depends not so much on the action of the root-system of grass, as on the accumulation of amorphous humus under perennial meadow vegetation.

#### SUMMARY

The interpretation of the form of the structural elements of chernozem soils can be based on the study of the decomposition of the complex mixed sand-clay-humus formations.

The form of the typical granular structure of chernozem is a sign of the accumulation of amorphous humus at the periphery of the aggregate.

Increase of the exchange capacity of soil must be closely connected with the appearance of amorphous humus at the periphery of the aggregate. If



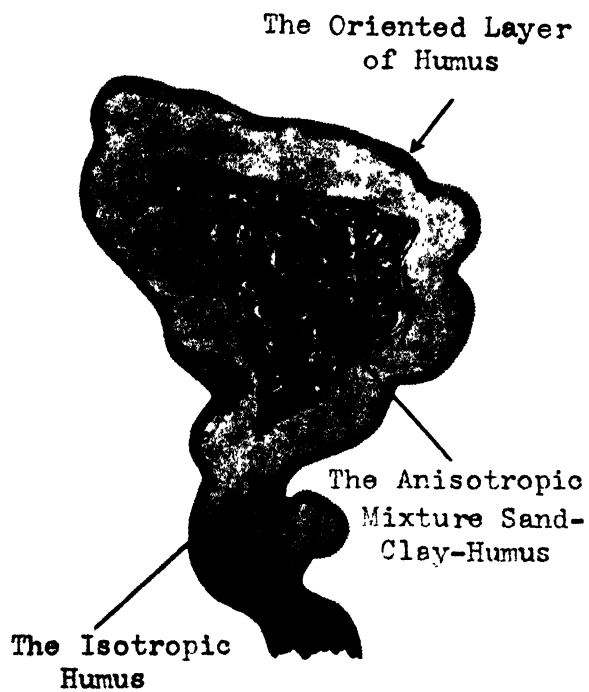
organic matter is firmly bound with clay as an anisotropic formation, no marked increase in the adsorption capacity occurs.

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#### PLATE 1

#### DISINTEGRATION OF THE SAND-CLAY-HUMUS MIXTURE





# THE EFFECT OF SHEEP AND GOAT MANURE ON SOME MEDITERRANEAN RED SOILS

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In a previous treatise one of the authors (6) dealt with the questions of why degradation is evident in Mediterranean red-sand soils and why the formation of "Nazaz" or "Pan" increases the degradation to such an extent as to render these soils uncultivable. The present investigation shows that an addition of organic fertilizer, in the form of sheep and goat manure, to these soils is capable of improving their physical properties and thus of counteracting the degradation. The procedure in arriving at this sequel comprised the following determinations: analyses of the sheep and goat manure; analyses of the soils; analyses of mixtures of the soils and manure; determination of the effects of the mixture on the physical and mechanical properties of the soils.

## ANALYSES OF SHEEP AND GOAT MANURE

Samples of goat and sheep manure from the Acre Stud Farm were examined in order to determine the differences in their chemical composition; the effect of the season on their composition; and the differences in their composition when the animals were grazed and when fed in the stall. This investigation was carried on for a year, covering the various seasons and the manifold ways in which the animals were fed. During this period eight consignments were received, each consisting of four samples, as follows: (A) sheep manure from stall, (B) sheep manure from field, (C) goat manure from stall, (D) goat manure from field.

Table 1 shows the analytical data on combined and free ammonia and total nitrogen in the fresh manure. The results were calculated on the fresh and on the moisture-free basis. On the air-dry samples, the following determinations were made: moisture, organic matter, combined  $\text{NH}_4$ , free  $\text{NH}_3$ , total nitrogen,  $\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}$ ; the ratio between organic matter and total nitrogen was also calculated. The methods of analyses adopted were as follows:

A 500-gm. portion of each sample was dried in the air until fit for crushing. A weighed portion of each of these air-dry samples was then oven-dried at 98–100°C. until constant weight was reached. The loss of moisture thus determined was calculated as percentage, and this was considered as the "moisture content of air-dry sample." Another 5-gm. portion

<sup>1</sup> The authors wish to express their thanks to the government analyst, G. W. Baker, for his advice and for correction of this paper.

of a mixed sample was similarly oven dried. This was considered as the "moisture-free sample."

Organic matter was determined (7) by igniting the manure and subtracting the moisture and ash, as suggested by Koenig. The accuracy of the determination was also checked by the direct method through wet oxidation.

The "free ammonia" was found by distilling 25 gm. of the fresh sample into 0.1 *N* H<sub>2</sub>SO<sub>4</sub>. The "combined ammonia" was found by using the same substance, adding to it 2 gm. of magnesium oxide, and distilling it again into 0.1 *N* H<sub>2</sub>SO<sub>4</sub>.

Total nitrogen was determined by the Kjeldahl method modified to include all the nitrates (1, p. 25).

P<sub>2</sub>O<sub>5</sub> was determined according to the A.O.A.C. method (1, p. 19). K<sub>2</sub>O was found by separating SO<sub>4</sub> and then by using the perchloric acid method.

TABLE 1  
*Analyses of sheep and goat manure\**

DESCRIPTION	FRESH SAMPLES				FRESH SAMPLES CALCULATED AS MOISTURE FREE		
	Moisture in air-dry sample	Combined NH <sub>4</sub>	Free NH <sub>3</sub>	Total nitrogen	Combined NH <sub>4</sub>	Free NH <sub>3</sub>	Total nitrogen
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A Sheep manure from stall . . . . .	58.4	0.027	0.144	0.8	0.079	0.423	2.35
B Sheep manure from field . . . . .	66.6	0.030	0.058	0.58	0.123	0.237	2.37
C Goat manure from stall . . . . .	60.2	0.019	0.088	0.7	0.061	0.285	2.27
D Goat manure from field . . . . .	63.2	0.023	0.064	0.65	0.084	0.234	2.38

*Air-dry samples calculated as moisture free*

SAMPLE	MOISTURE AT 100°C.	ORGANIC MATTER	COMBINED NH <sub>4</sub>	FREE NH <sub>3</sub>	TOTAL NITROGEN	RATIO ORGANIC MATTER TO TOTAL N†	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
A	7.6	74.2	0.021	0.051	2.0	37.1	1.83	0.77
B	9.0	73.6	0.043	0.036	2.0	36.8	1.76	0.76
C	9.0	76.2	0.022	0.025	2.1	36.3	1.56	0.68
D	9.5	75.4	0.023	0.024	2.1	35.9	1.50	0.69

\* Every figure represents the average of eight determinations made on consecutive dates.

† Total nitrogen = 1.

The following conclusions may be drawn from table 1:

In drying, the organic manure loses some of its nitrogen.

More "free ammonia" is produced by feeding the animals in stalls than by grazing.

There is no marked difference between goat and sheep manure in percentages of all other constituents.

#### ANALYSES OF THE SOILS

In order to have a rather varied representation of soils, two samples were obtained, one from the hilly land of Rehovoth in the south of Palestine, and the other from the marshy land of Hederah in the north. The first sample

consisted of red-sand soil, poor in lime (less than 1.5 per cent); and since the profile was homogeneous, it was taken from a depth ranging between 0 and 100 cm. The second consisted of dark-red heavy soil, also poor in lime (less than 1.5 per cent), homogeneous, and from a depth of 0 to 100 cm.

Table 2 shows the results of the mechanical and physical determinations of these soils. The mechanical analyses were determined according to Beam (2); the water-holding capacity, according to Keen (4); the wilting point, according to Briggs and McLane (3). The moisture equivalent of the sample was determined by centrifuging, and then dividing the result by 1.84. After the true and the apparent specific gravities were determined, the pore space

TABLE 2  
*Analyses of soil samples*

SAMPLE	MOIS- TURE AT 100°C.	MECHANICAL ANALYSIS*				PHYSICAL DETERMINATIONS					
		Clay	Silt	Fine sand	Coarse sand	Water-holding capacity	Wilting point†	True specific gravity (a)	Apparent specific gravity (b)	Pore space‡	Water permeability§
	per cent	per cent	per cent	per cent	per cent	per cent					
Heavy soil from Hederah . .	9.0	61.0	9.6	20.0	9.4	54.3	24.9	2.41	1.43	40.0	1,714 hours
Light soil from Rehovoth. .	4.2	22.4	2.4	20.2	55.0	37.0	16.5	2.64	1.53	42.0	67 hours, 40 min.

\* According to Beam (2), Soudan method.

† Moisture equivalent.

L84

$$\ddagger \frac{a-b}{a} \times 100.$$

§ Hours per liter.

was calculated by the formula  $\frac{a-b}{a} \times 100$  (where  $a$  = true specific gravity;  $b$  = apparent specific gravity). The water permeability was expressed in hours per liter. These data were carefully considered in order to show the change in the mechanico-physical properties after the addition of organic substances.

#### ANALYSES OF MIXTURES OF SOIL AND MANURE

The samples of manure, which did not vary greatly in composition, were combined and ground, and one part was mixed with four parts of the soil. The water optimum was considered to be the mean value between the wilting point and the water-holding capacity. The water optimum was maintained

during the experiment, the daily loss being determined, and the amount evaporated being replaced. The mixture, spread in a thin layer, was kept in the open air to ensure thorough decomposition. The carbon and the nitrogen were determined after every fortnight until constant values were obtained, and the results as moisture-free were calculated. For the calculation of carbon, the organic matter was determined, and the result was multiplied by 0.58. From the analytical data, given in table 3, the following facts are apparent:

C diminishes rapidly in the first 2½ months, whereas N changes very little in the same interval;

C decomposes gradually during the remaining 3½ months, whereas N remains constant;

At the end of 6 months, the two constituents remain almost constant.

TABLE 3  
*Carbon and nitrogen contents of mixtures of soils and manure*

DATES, 1937	HEAVY SOIL			LIGHT SOIL		
	Carbon	Total N	Ratio* C/N	Carbon	Total N	Ratio* C/N
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>	
July 1 . . . . .	8.0	0.34	23.5	5.9	0.28	21.1
14 . . . . .	7.1	0.34	20.9	6.4	0.31	20.6
August 1. . . . .	6.6	0.32	20.6	5.3	0.30	17.6
14 . . . . .	6.0	0.30	20.0	4.5	0.27	16.7
September 1. . . . .	5.4	0.28	19.3	3.9	0.26	15.0
14 . . . . .	4.9	0.27	18.1	3.8	0.25	15.2
October 1. . . . .	4.2	0.27	15.6	3.1	0.25	12.4
14 . . . . .	4.0	0.27	14.8	2.7	0.24	11.2
November 1. . . . .	3.8	0.27	14.0	2.8	0.24	11.7
14 . . . . .	3.3	0.27	12.2	2.6	0.24	10.9
December 1. . . . .	3.2	0.27	11.9	2.7	0.24	11.2
14 . . . . .	3.3	0.27	12.2	2.6	0.24	10.9

\* Total nitrogen = 1.

#### EFFECTS OF MIXTURE ON PHYSICAL AND MECHANICAL PROPERTIES OF SOILS

Table 4 shows how the mechanical and physical properties of the soils have been changed as a result of the mixture with manure. Addition of organic fertilizers diminishes the clay content of heavy soils but does not appreciably change that of light soils. The following noteworthy changes occur in the physical properties:

The water-holding capacity, as well as the wilting point, rises in both the light and the heavy soils;

The pore space increases;

The water permeability becomes more advantageous in both soils. In the heavy soils, without the addition of organic substances, the time of permeability of 1 liter of water is 1,714 hours; after addition of manure, this period diminishes to 1,200 hours. In the light soils, however, the addition of organic substances prolongs the time of permeability from 67 hours and 40 minutes to 90 hours.

Table 5, essentially a comparative table, gives analytical data of exchangeable bases obtained before the addition of manure and after the addition had resulted in a constant C/N ratio. The soils were freed from the cations Ca, Mg, K, and Na by means of a 0.05 *N* HCl solution; washed with distilled water until they were free from chlorine; and dried until they became water-free. These base-free soils were then shaken for 48 hours with a solution of *N* BaCl<sub>2</sub> (1:5), filtered, washed again until they were free from chlorine, dried, and Ba-regenerated, then evaporated to a small volume, precipitated with H<sub>2</sub>SO<sub>4</sub>, washed, filtered, and ignited to a constant weight. The result was expressed as milliequivalents of Ba. Table 5 shows that the Ba content of the light soil

TABLE 4  
*Analyses\* of mixtures of soil and manure*

SAMPLE	MOISTURE AT 100°C.	MECHANICAL ANALYSIS				PHYSICAL DETERMINATIONS					
		Clay	Silt	Fine sand	Coarse sand	Water-holding capacity	Wilting point	True specific gravity	Apparent specific gravity	Pore space	Water permeability
	per cent	per cent	per cent	per cent	per cent	per cent					hours
Heavy soil from Hederah . . .	7.9	49.4	14.0	19.6	17.0	75.9	34.6	1.85	1.00	45.0	1,200
Light soil from Rehovoth	3.2	22.4	6.4	16.6	54.6	63.0	29.1	1.93	1.03	46.0	90

\* See footnotes to table 2.

TABLE 5  
*Exchangeable bases in soils before and after addition of manure*

DESCRIPTION AND SOURCE	Ba
	m.e.
Light soil from Rehovoth without manure . . . . .	6.6
Light soil from Rehovoth with organic manure . . . . .	14.6
Heavy soil from Hederah without manure . . . . .	28.5
Heavy soil from Hederah with organic manure . . . . .	38.5

increases from 6.6 to 14.6 m.e.; and that of the heavy soil, from 28.5 to 38.5 m.e. These figures agree with the values arrived at by McGeorge (5) and Turner (8), who concluded that for 10 gm. of C in the soil, the exchangeability increases by 35 m.e.; according to our results it increases by 30.3 m.e. in heavy soils and 30.7 m.e. in light soils.

#### CONCLUSIONS

The analyses of the sheep and goat manure show that the composition is not materially affected by either the seasons or by the variation and manner of feeding. On drying the manure, some loss of nitrogen is observed.



The decomposition of the manure, as indicated by the C/N ratio, appears to have been completed in 6 months, under laboratory conditions in which the soil was kept at constant moisture content.

The C/N ratio of "humus-like" substances and the increase of the value of exchangeable bases as a result of the proportional increase of C are similar to results obtained by other investigators.

The addition of organic substances not only enhances the supply of such nutritives as K, N, and  $P_2O_5$  to the soils and improves the physical properties, in general, but increases also the exchangeable bases.

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# ECONOMICAL USES OF FERTILIZER ELEMENTS BY CERTAIN FORAGE CROPS<sup>1</sup>

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Earlier workers (1, 3) of the Rhode Island Agricultural Experiment Station investigated the fertilizer nutrient requirements of cereals grown in solution and soil cultures in the greenhouse. Minimum percentages of nitrogen, phosphorus, and potassium which brought about satisfactory growth and yields of grain and straw by barley, oats, and wheat were established. With the increased interest developing in the northeastern dairy regions of the United States in pasture improvement problems, the emphasis in research shifts from cereals to forage crops, and the need of more definite knowledge as to methods of stimulating the growth of pasture grasses is apparent. Little or no work, comparable to the experiments with cereals, seems to have been done with redbot, timothy, or colonial bent.

## GROWTH METHODS

Essentially the same technic as that used by former workers at this station with cereals was followed in a study of the nutrient requirements of timothy, redbot, and colonial bent (R. I. Bent). This technic, established by Pember (3), has been described in detail by Pember and McLean (4). It is unnecessary, therefore, to go into detail in the description of the growth methods followed, except in those points where minor changes were made.

In the previous work with cereals, considerable care was taken to obtain yields of grain. As the vegetative portions of the forage crops are of greatest value, dates of harvesting were chosen, with both solution and soil cultures, to correspond with the maximum vegetative yields of the crops studied.

## *Solution cultures*

Each culture contained only 10 plants and was grown in triplicate. The seedlings were carefully selected as to uniformity and were grown in nutrient solution (4) from January to May of each year. The fertilizer nutrients were varied in each culture solution in an endeavor to produce optimum and sub-optimum conditions.

<sup>1</sup> Published, by permission of the director of research, as Contribution No. 526 of the Rhode Island Agricultural Experiment Station.

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In order to safeguard against the possibility of limiting conditions due to very low concentrations of the minor elements, at each change of solution small amounts of magnesium sulfate, ferric nitrate, manganese sulfate, and sodium borate [4 cc. 0.1 *M*  $\text{MgSO}_4$ , 1.18 gm. per liter of  $\text{Fe}(\text{NO}_3)_3$ , 1 p.p.m. Mn, and 1 p.p.m. B] were added. The tillers were clipped from all cultures weekly and were dried and weighed separately from the tops and roots.

### *Soil cultures*

Timothy, redtop, and colonial bent were grown in soil cultures in Wagner pots with varying amounts of  $\text{K}_2\text{O}$ , N, and  $\text{P}_2\text{O}_5$  applied in fertilizer salts. In 1931 and 1932 the soil used for the potash series was taken from plat 116 of the agronomy farm. This plat is considered to be very low in residual potash. For the nitrogen series, the soil from plat 116 was used in 1931; and then, since there may have been some nitrogenous residue from organic matter, soil from a fallow area was used in 1932. For the phosphorus series in both years soil from plat 67, which is the low-phosphorus plat of the phosphate series of agronomy plats, was used.

All the  $\text{P}_2\text{O}_5$  was applied as superphosphate (21.7 per cent  $\text{P}_2\text{O}_5$ ) at the beginning of the experiments. The  $\text{K}_2\text{O}$  was applied as  $\text{K}_2\text{SO}_4$  (49.9 per cent  $\text{K}_2\text{O}$ ) at intervals during the growth of the cultures, and the nitrogen was also applied at intervals as  $\text{NaNO}_3$  (16.2 per cent N), the first application of each being made when the plants were transplanted to the pots.

After being harvested, the plants were air-dried and weighed.

### PRESENTATION OF DATA

Though several workers have studied the response to fertilizer nutrients of redtop and timothy when grown under field conditions, few attempts have been made to study either these forage crops or colonial bent under such controlled conditions as can be secured in solution or soil cultures under glass. The dry weights of the cultures grown in these experiments show some interesting results.

### *Solution cultures*

Table 1 presents the total nutrients added, in grams per culture, and the dry weight yields of roots, tops, and clips of timothy, redtop, and colonial bent grasses grown in culture solutions. The average relative yields are included so that it is possible to determine readily the relationships which may exist between fertilizer nutrients and yields.

It will be noted that all crops responded most to potash insofar as roots were concerned. The tops of colonial bent and redtop were affected most by the extra amounts of nitrogen. Timothy tops seemed to benefit most from the increased quantities of potash in the solution. When the clippings for all crops were considered, the low-nitrogen cultures gave the lowest weights.

TABLE 1

*Nutrients added and dry weight yields of timothy, redtop, and colonial bent grown in culture solutions*

	NUTRIENTS ADDED, PER CULTURE			DRY WEIGHT YIELDS			AVERAGE RELATIVE YIELDS FOR TWO CROPS			
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Roots	Tops	Clips	Roots	Tops	Clips	Top and clip
	gm.	gm.	gm.	gm.	gm.	gm.				
<i>Colonial bent</i>										
<i>1931</i>										
Complete NPK . . . . .	.269	.091	.199	7.4	11.7	3.9	100	100	100	
Low N . . . . .	.061	.091	.199	5.4	4.9	2.0	78	45	48	
Low P . . . . .	.269	.017	.199	4.9	5.4	2.3	71	52	59	
Low K . . . . .	.269	.091	.042	3.3	8.4	2.9	38	62	70	
<i>1935</i>										
Complete NPK . . . . .	.280	.116	.216	5.6	8.8	4.4				
Low N . . . . .	.076	.116	.216	4.8	4.4	2.0				
Low P . . . . .	.280	.021	.216	4.3	5.3	2.6				
Low K . . . . .	.280	.116	.036	1.7	4.4	2.9				
<i>Timothy</i>										
<i>1931</i>										
Complete NPK . . . . .	.398	.128	.268	11.5	19.2	5.2	100	100	100	100
Low N . . . . .	.116	.128	.268	9.0	15.3	2.3	83	72	43	69
Low P . . . . .	.398	.020	.268	8.1	10.0	2.2	71	67	41	63
Low K . . . . .	.398	.128	.047	3.2	7.2	5.1	37	48	94	54
<i>1935</i>										
Complete NPK . . . . .	.304	.122	.234	7.9	30.2	1.7				
Low N . . . . .	.088	.122	.234	7.1	20.3	0.7				
Low P . . . . .	.304	.021	.234	5.7	22.9	0.6				
Low K . . . . .	.304	.122	.036	4.0	16.6	1.4				
<i>Redtop</i>										
<i>1931</i>										
Complete NPK . . . . .	.271	.091	.194	9.5	9.8	5.4	100	100	100	100
Low N . . . . .	.071	.091	.194	5.9	3.8	2.5	69	46	52	48
Low P . . . . .	.271	.021	.194	6.9	5.8	2.8	75	61	49	57
Low K . . . . .	.271	.091	.042	2.7	4.3	4.5	35	50	83	61
<i>1935</i>										
Complete NPK . . . . .	.312	.125	.240	8.6	9.2	3.8				
Low N . . . . .	.092	.125	.240	6.5	5.0	2.3				
Low P . . . . .	.312	.021	.240	6.6	5.8	1.7				
Low K . . . . .	.312	.125	.036	3.6	5.2	3.1				

When weights of tops and clips were averaged, the greatest response was obtained with nitrogen in the cultures of colonial bent and red top, and with potash in the cultures of timothy. This reaction of timothy to potash is of

TABLE 2

*Nutrients added and dry weight yields of timothy, redtop, and colonial bent grown in soil cultures*

	NUTRIENTS ADDED, PER CULTURE			DRY WEIGHT YIELDS			AVERAGE RELATIVE YIELDS		
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Tops	Clips	Total	Tops	Clips	Total
	gm.	gm.	gm.	gm.	gm.	gm.			
<i>Redtop</i>									
<i>1931</i>									
No N . . . . .	.0	1.085	1.248	1.3	1.5	2.8	22	18	20
1 N . . . . .	.081	1.085	1.248	1.8	2.8	4.6	30	34	32
2 N . . . . .	.162	1.085	1.248	2.8	3.9	6.7	47	47	47
3 N . . . . .	.405	1.085	1.248	6.0	8.3	14.3	100	100	100
No P . . . . .	.405	0.0	1.248	6.3	5.5	11.8	105	66	83
1 P . . . . .	.405	0.217	1.248	4.8	6.4	11.2	80	77	78
2 P . . . . .	.405	0.434	1.248	5.5	6.8	12.3	92	82	86
3 P . . . . .	.405	1.085	1.248	6.0	8.3	14.3	100	100	100
No K . . . . .	.405	1.085	0.0	5.5	6.6	12.1	115	96	103
1 K . . . . .	.405	1.085	1.250	5.0	6.8	11.8	104	99	101
2 K . . . . .	.405	1.085	0.998	4.5	6.5	11.0	94	94	94
3 K . . . . .	.405	1.085	1.248	4.8	6.9	11.7	100	100	100
<i>1932</i>									
No N . . . . .	.0	1.092	1.440	1.5	2.8	4.3	21	34	28
1 N . . . . .	.081	1.092	1.440	3.8	3.8	7.6	54	46	50
2 N . . . . .	.162	1.092	1.440	6.5	4.9	11.4	93	60	75
3 N . . . . .	.324	1.092	1.440	7.0	8.2	15.2	100	100	100
No P . . . . .	.324	0.0	1.440	5.0	4.0	9.0	125	50	75
1 P . . . . .	.324	0.219	1.440	5.8	7.5	13.3	145	94	111
2 P . . . . .	.324	0.437	1.440	8.0	7.6	15.6	200	95	130
3 P . . . . .	.324	1.092	1.440	4.0	8.0	12.0	100	100	100
No K . . . . .	.324	1.092	0.0	5.0	8.6	13.6	116	100	105
1 K . . . . .	.324	1.092	0.240	7.5	7.9	15.4	174	92	119
2 K . . . . .	.324	1.092	0.960	9.4	6.9	16.3	219	80	126
3 K . . . . .	.324	1.092	1.440	4.3	8.6	12.9	100	100	100
<i>Colonial bent</i>									
<i>1931</i>									
No N . . . . .	.0	1.085	1.248	2.0	1.5	3.5	35	23	29
1 N . . . . .	.081	1.085	1.248	4.5	2.2	6.7	78	34	55
2 N . . . . .	.162	1.085	1.248	6.3	3.3	9.6	109	52	79
3 N . . . . .	.405	1.085	1.248	5.8	6.4	12.2	100	100	100
No P . . . . .	.405	0.0	1.248	2.0	3.0	5.0	34	47	41
1 P . . . . .	.405	0.217	1.248	4.0	4.8	8.8	69	75	72
2 P . . . . .	.405	0.434	1.248	2.8	4.4	7.2	48	69	59
3 P . . . . .	.405	1.085	1.248	5.8	6.4	12.2	100	100	100
No K . . . . .	.405	1.085	0.0	10.0	6.0	16.0	102	120	108
1 K . . . . .	.405	1.085	0.250	6.0	5.2	11.2	61	104	76
2 K . . . . .	.405	1.085	0.998	7.8	5.3	13.1	80	106	89
3 K . . . . .	.405	1.085	1.248	9.8	5.0	14.8	100	100	100

TABLE 2—*Concluded*

	NUTRIENTS ADDED, PER CULTURE			DRY WEIGHT YIELDS			AVERAGE RELATIVE YIELDS		
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Tops	Clips	Total	Tops	Clips	Total
	gm.	gm.	gm.	gm.	gm.	gm.			
<i>Colonial bent—Continued</i>									
<i>1932</i>									
No N . . . . .	.0	1.092	1.440	4.0	1.4	5.4	36	25	32
1 N . . . . .	.081	1.092	1.440	6.5	2.1	8.6	59	37	51
2 N . . . . .	.162	1.092	1.440	9.5	3.1	12.6	86	54	75
3 N . . . . .	.324	1.092	1.440	11.0	5.7	16.7	100	100	100
No P . . . . .	.324	0.0	1.440	4.0	3.2	7.2	38	64	46
1 P . . . . .	.324	0.219	1.440	12.0	3.9	15.9	114	78	103
2 P . . . . .	.324	0.437	1.440	8.5	3.9	12.4	81	78	80
3 P . . . . .	.324	1.092	1.440	10.5	5.0	15.5	100	100	100
No K . . . . .	.324	1.092	0.0	8.5	5.3	13.8	85	82	84
1 K . . . . .	.324	1.092	0.240	10.8	4.7	15.5	108	72	94
2 K . . . . .	.324	1.092	0.960	11.5	4.9	16.4	115	75	99
3 K . . . . .	.324	1.092	1.440	10.0	6.5	16.5	100	100	100
<i>Timothy</i>									
<i>1931</i>									
No N . . . . .	.0	1.085	1.248	3.0	2.2	5.2	14	38	20
1 N . . . . .	.081	1.085	1.248	4.3	3.5	7.8	21	60	30
2 N . . . . .	.162	1.085	1.248	8.8	4.5	13.3	43	78	51
3 N . . . . .	.405	1.085	1.248	20.3	5.8	26.1	100	100	100
No P . . . . .	.405	0.0	1.248	8.8	0.7	9.5	43	12	36
1 P . . . . .	.405	0.217	1.248	16.8	3.3	20.1	83	57	77
2 P . . . . .	.405	0.437	1.248	22.8	4.6	27.4	112	79	105
3 P . . . . .	.405	1.085	1.248	20.3	5.8	26.1	100	100	100
No K . . . . .	.405	1.085	0.0	20.3	6.5	26.8	108	90	103
1 K . . . . .	.405	1.085	0.250	18.8	6.7	25.5	100	93	98
2 K . . . . .	.405	1.085	0.998	18.5	7.2	25.7	98	100	99
3 K . . . . .	.405	1.085	1.248	18.8	7.2	26.0	100	100	100
<i>1932</i>									
No N . . . . .	.0	1.092	1.440	3.8	1.4	5.2	17	15	17
1 N . . . . .	.081	1.092	1.440	8.0	3.0	11.0	37	32	35
2 N . . . . .	.162	1.092	1.440	11.5	4.1	15.6	53	44	50
3 N . . . . .	.486	1.092	1.440	21.8	9.4	31.2	100	100	100
No P . . . . .	.486	0.0	1.440	12.0	4.7	16.7	73	53	66
1 P . . . . .	.486	0.219	1.440	15.0	6.7	21.7	91	76	86
2 P . . . . .	.486	0.437	1.440	13.0	8.0	21.0	79	91	83
3 P . . . . .	.486	1.092	1.440	16.5	8.8	25.3	100	100	100
No K . . . . .	.486	1.092	0.0	21.3	6.8	28.1	164	79	130
1 K . . . . .	.486	1.092	0.240	17.8	7.1	24.9	137	83	115
2 K . . . . .	.486	1.092	0.960	17.0	8.4	25.4	131	98	118
3 K . . . . .	.486	1.092	1.440	13.0	8.6	21.6	100	100	100

interest because it seems to be at variance with the usual concept of the responses of grasses to fertilizer elements. It should be recognized that the prevailing knowledge is based on fertilizer trials under field conditions. The data presented here may be considered as picturing more nearly the absolute relative minimum requirements of these three crops. The amounts of nutrients available to the plant in a culture solution are, in many instances, relatively less than those in fertilized soil, and in this set of experiments these amounts were planned to approximate starvation levels.

### *Soil cultures*

In the light of the foregoing results, it is of interest to compare timothy, redbtop, and colonial bent when growing in soil and with additional nutrients supplied at varying levels. Table 2 gives the nutrients applied and the dry weight and average relative yields of these three forage crops when grown under such conditions.

It will be noted that the response of all three crops, in tops, clips, and total yields, was greatest to nitrogen. Response to phosphorus, although evident, was not so marked or regular as response to nitrogen. There were indications of but slight response to potash, even with timothy, which responded markedly in the solution cultures. These results are similar to those obtained by North and Odland (2) in a study of the seed yields of colonial bent as affected by fertilization under field conditions. They note that "Phosphorus and potash produced little effect on the growth . . ."

These results with soil cultures seem to show that, even under what would be considered low nutrient conditions, timothy, redbtop, and colonial bent are able to produce optimum growth, provided sufficient nitrogen is supplied. They also seem to show that, though conditions in the solution cultures so closely approached starvation levels for potash and phosphorus that growth was reduced, such conditions were not approached in these soil cultures.

It should be noted that these experiments were conducted in pots with one soil type only and under conditions which may not have been entirely comparable to field conditions. Other investigators have obtained results which seem to show that both phosphate and potash are helpful in stimulating vegetative growth of grasses in the field, particularly when used in conjunction with lime. No attention was given in these experiments to the importance of the composition of the forage and to its nutritive value, which under field conditions would be greatly increased by applications of phosphoric acid and potash.

### SUMMARY

This study reports the comparative dry weight yields of cultures of timothy, colonial bent, and redbtop, grown in solution and soil cultures with varying levels of fertilizer elements.

*Solution culture results.* With all the crops, root growth was increased by greater amounts of potash. The clippings or tiller growth was stimulated by

extra nitrogen. The weight of tops of colonial bent and of redtop was greatest with the higher amounts of nitrogen, and that of timothy tops was greatest with extra potash. The lowest culture conditions were near the absolute mineral nutrient requirements of these crops.

*Soil culture results.* All three crops responded best, in tops, clips, and total yields, to the higher nitrogen applications. The response to phosphorus was less marked than the response to nitrogen, and but slight indications of response to potash were obtained with any of the crops grown on one soil type only. It is concluded that colonial bent and redtop require less potash and phosphorus for good growth than does timothy and that all three crops require high fertilization with nitrogen.

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# EFFECT OF "ALKALI" SALTS ON GENERAL MICROBIAL FUNCTION IN SOIL

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Soil bacteria, as well as higher plants, are affected by so-called "alkali" salts; this has been recognized since the pioneer work of C. B. Lipman (11). The problems of reclamation of natural saline soils and the prevention of salinization of soils now in cultivation have led to many investigations on the effects of "alkali" salts on biological as well as physical and chemical properties of the soil.

## HISTORICAL

In studies on ammonification, Lipman (10, 12) demonstrated relatively high toxicity of sodium sulfate and stimulation by sodium carbonate; he also found "antagonism" or reduction in toxicity with combinations of sodium, potassium, and magnesium chlorides, and with chloride, sulfate, and carbonate of sodium. From laboratory and greenhouse tests on a normal soil and on a saline soil, Brown and Hitchcock (2) concluded that nitrification and crop growth are similarly affected by "alkali" salts, low concentrations being stimulating, and high concentrations, with the exception of calcium carbonate, being depressive. Brown and Johnson (3) found that ammonification was markedly stimulated by 0.6 per cent calcium carbonate but was inhibited by 0.1 per cent sodium bicarbonate, 0.2 per cent sodium carbonate, and 0.5 per cent sodium sulfate.

In a series of studies by Greaves (6, 8), soil texture and moisture were found to influence the relative toxicity of various salts. Greater toxicity was exerted in a sandy soil than in a loam soil, and toxicity decreased as moisture increased. Small quantities of salts added to a soil increased bacterial activities, as indicated by increased ammonification, nitrification, and nitrogen fixation (7). Toxicity of the various salts was found closely proportional to the osmotic pressure produced in the soil, showing that toxicity is partly due to osmotic disturbance. Another factor advanced as preventing bacteria from performing their natural functions is the physiological influence of a given salt; this is determined not alone by the concentration of salt in the soil, but also by cell permeability and the physical-chemical influence of the salt upon

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the protoplasm. Nitrifiers were found to be more sensitive than ammonifiers, whereas the nonsymbiotic nitrogen-fixers were found to be more resistant, tolerating higher concentrations of "alkali" and other salts than do most higher plants.

Comparing ammonification, nitrification, and crop yield during production of two crops of wheat with percentage recovery of added salts in a neutral silt loam soil, Gibbs, Batchelor, and Magnuson (5) found a general tendency for any toxic action to disappear as time progressed. This was in line with the gradual decrease in total water-soluble salts; however, neither toxic nor stimulating action was proportional to total salt recovery. Although sodium carbonate was toxic to plant growth, it stimulated ammonification of blood and nitrification of ammonium sulfate; in general, sodium chloride had the reverse influence, and sodium sulfate had only slight effect.

#### OBJECT OF INVESTIGATION

These previous investigations have been concerned with specific groups of soil bacteria; so far as is known, similar studies on the more generalized function of organic decomposition and carbon dioxide production have not been reported. This phase of the alkali problem was attacked through the study of decomposition of native and incorporated organic matter in an acid soil treated with "alkali" salts, and in a virgin saline soil and its partially reclaimed counterpart.

#### METHODS

Carbon dioxide evolution during incubation at room temperature and optimum moisture content in a respiration apparatus similar to that described by Potter and Snyder (14) was used as an index of general microbial activity and organic decomposition. In the apparatus used, however, the  $\text{CO}_2$ -free air was passed over the soil by slight pressure rather than by suction, and in this way the pressure over the soil, as well as over the absorbing solution, was maintained at approximately one atmosphere. The  $\text{CO}_2$  evolved was absorbed in approximately  $N$  NaOH and determined by double titration, phenolphthalein and brom-phenol-blue being used as indicators. Results are expressed as milligrams of carbon evolved as  $\text{CO}_2$  per kilogram of soil on the water-free basis. Values for the check or untreated soil were subtracted from values for the treated soils in the plotting of all results. The curve for the check is thus plotted as the x-axis. This not only reduces the size of the graph but also presents the data in more striking form.

Chemical and microbial analyses were also made to determine changes in water-soluble anions and in pH, and in numbers of molds, bacteria, actinomyces, and *Azotobacter* cells. A 1:5 suspension of the soil was prepared with sterile distilled water and shaken for 30 minutes; the coarser particles were then allowed to settle, and a 1-cc. sample was withdrawn for the preparation

of dilutions for plate counts. Determination of pH, by means of circulating hydrogen electrode (1), was made on another portion. The remaining suspension was then filtered through a Pasteur-Chamberland candle, and the filtrate was analyzed. Association of Official Agricultural Chemists methods of analysis for waters were used for the determination of nitrate, nitrite, chloride, carbonate, and bicarbonate. Sulfate was determined by the turbidity method of Schreiner and Failyer (16). Truog and Meyer's modification (17) of the Deniges method for phosphate was used.

In the microbial counts, peptone-glucose-acid agar was used for molds, and sodium albuminate agar as described by Fred and Waksman (4) was used for bacteria and actinomyces. Duplicate plates from appropriate dilutions were poured in 150-mm. petri dishes; the number of colonies counted after incubation at 28°C. ranged from approximately 50 to 250. Numerous control plates, amounting to at least 10 per cent of the total poured, were used. *Azotobacter* was determined by the soil-paste plaque method, 5 per cent starch and 1 per cent powdered  $\text{CaCO}_3$  being used.

#### EFFECTS OF ADDED "ALKALI" SALTS

To determine the effects of added "alkali" salts on the microbial population and its activities, the following experiment was made with Willamette silty clay loam. This is nonsaline slightly acid soil of great agricultural importance in the subhumid Willamette Valley region. A bulk sample, taken along a fence and believed to be essentially "virgin," was passed through a 2-mm. sieve and mixed. The moisture content after mixing was 21 per cent. Saturation capacity, as determined by the amount of water held against gravity by a portion saturated in a gooch and allowed to drain in a saturated atmosphere, was 52 per cent. Kjeldahl nitrogen was 0.260 per cent, and organic matter by Rather's (15) method, 4.01 per cent.

One-kilogram portions were treated with "alkali" salts alone, in combination with ground wheat straw, and in combination with wheat straw plus sodium nitrate, as indicated in figure 1. The 2 per cent concentration of salts added is excessive from the standpoint of plant tolerance, as well as for certain soil microbial functions, as has been determined by previous investigators. This concentration was used, however, in order to obtain a maximum effect on the more generalized activities which may be expected to persist even in soils containing still higher concentrations. Sodium nitrate, added in small amount with the straw in several treatments, was used in order to avoid lack of available nitrogen as a factor retarding decomposition.

Each treated portion of soil was placed in a 2.5-liter bottle, distilled water was added to bring the soil moisture to 60 per cent of the saturation capacity, and the bottle was then connected to the respiration apparatus. Carbon dioxide evolution was determined during 164 days, titrations being made at daily intervals during the first 10 days, after which longer and longer intervals were used until the final determination represented a 30-day period. Chemical



whether added alone or in various combinations. Sodium carbonate thus retarded decomposition of the straw in all cases, its effect being intermediate as compared to sodium sulfate and magnesium sulfate. That it also retarded decomposition of the native organic matter is indicated by the latter portion of curve 3, figure 1, which shows a negative slope.

Sodium nitrate slightly increased the decomposition of straw, except in combination with sodium carbonate. It is hardly probable that the sodium concentration may have been critical, so that the 34 p.p.m. from the nitrate, added to the 8,680 p.p.m. supplied by the carbonate, produced the marked decrease in  $\text{CO}_2$  evolution. Although there is ample evidence that nitrate additions increase decomposition of organic matter of wide carbon-nitrogen ratio, it has been occasionally observed that inorganic nitrogen compounds decrease  $\text{CO}_2$  evolution. A stimulation of autotrophes and their assimilation

TABLE 1  
*Carbon balance in carbonate-treated Willamette silty clay loam*  
After 164 days' respiration

TREATMENT	C ADDED			C AS CO <sub>2</sub>	C AS HCO <sub>3</sub>	C EVOLVED FROM SOIL AS CO <sub>2</sub>				C OF STRAW EVOLVED AS CO <sub>2</sub>
	CO <sub>2</sub>	Straw	Total			Total	From additions	From additions plus C as HCO <sub>3</sub>	From straw	
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	per cent
Check . . . . .	0	0	0	0	5	1,250				
Straw . . . . .	0	2,500	2,500	0	10	2,000	750	760	755	30
Na <sub>2</sub> CO <sub>3</sub> . . . . .	2,260	0	2,260	160	702	2,280	1,030	1,732		
Straw + Na <sub>2</sub> CO <sub>3</sub> . . . . .	2,260	2,500	4,760	180	670	2,890	1,640	2,310	578	23
Straw + Na <sub>2</sub> CO <sub>3</sub> + NaNO <sub>3</sub> . . . . .	2,260	2,500	4,760	190	670	2,755	1,505	2,175	443	18

of  $\text{CO}_2$  may account for this; a discussion of this point in connection with other data will be presented in a later paper. It is significant that in all cases added nitrate was apparently assimilated, the amounts recovered at the close of the experiment being the same as or less than those in soil correspondingly treated but without nitrate addition.

Results of analyses of water extracts made at the close of the experiment are given in table 2. Nitrates are significantly low in every salt-treated sample, especially where carbonate and chloride were added. Magnesium sulfate and sodium sulfate had less effect, in the order named. These results correlate closely with the trend of  $\text{CO}_2$  evolution as influenced by the same salts; thus nitrates were higher in the presence of sodium sulfate, which was least depressive to  $\text{CO}_2$  production. This relation, however, does not necessarily indicate direct influence on nitrification, since after greater decomposition more nitrates should appear. Moreover, the nitrate concentration was virtually the same

in all samples treated with a given salt, regardless of straw or nitrate additions, and since salt additions in all cases caused a marked decrease in nitrates, either nitrate assimilation or denitrification was stimulated. Denitrification was unlikely, because aerobiosis was maintained and because the nitrite concentration was low in all cases.

Reduction in phosphate concentration occurred in all the salt-treated soils and corresponded closely with pH changes, sodium carbonate exerting the greatest effect. Although the actual amount of water-soluble phosphate is low, even in the untreated soil, it is indicative of at least an immediately ample supply of available phosphorus.

TABLE 2

*Effect of treatments on composition of water extract from Willamette silty clay loam*

After 160 days' incubation

TREATMENT	N AS NO <sub>3</sub>	N AS NO <sub>2</sub>	P AS PO <sub>4</sub>	Cl	S AS SO <sub>4</sub>	C AS CO <sub>3</sub>	C AS HCO <sub>3</sub>	pH
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	
Original sample . . . . .	30.0	0.1	2.0	Trace	2	0	3	6.20
0. No treatment . . . . .	75.0	0.3	3.3	"	30	0	5	6.33
1. Straw—5 T.* . . . .	75.0	0.4	3.3	"	29	0	10	6.54
2. Straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . .	60.0	0.3	2.5	"	29	0	7	6.72
3. Na <sub>2</sub> CO <sub>3</sub> —2 per cent. . . . .	2.5	0.7	1.5	"	30	180	702	8.43
4. Na <sub>2</sub> CO <sub>3</sub> —2 per cent, straw—5 T. . .	2.0	0.9	1.5	"	30	180	670	8.52
5. Na <sub>2</sub> CO <sub>3</sub> —2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	2.0	0.6	1.6	"	30	190	670	8.52
6. NaCl—2 per cent. . . . .	2.5	0.6	1.7	10,600	30	0	7	7.32
7. NaCl—2 per cent, straw—5 T. . . .	2.5	2.5	2.0	10,800	30	0	12	7.43
8. NaCl—2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	2.5	1.8	2.0	10,800	30	0	10	7.43
9. Na <sub>2</sub> SO <sub>4</sub> —2 per cent . . . . .	10.0	0.5	2.5	Trace	4,890	0	12	7.31
10. Na <sub>2</sub> SO <sub>4</sub> —2 per cent, straw—5 T. . .	25.0	0.8	2.5	"	3,930	0	12	7.33
11. Na <sub>2</sub> SO <sub>4</sub> —2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	10.0	0.8	2.5	"	4,740	0	10	7.33
12. MgSO <sub>4</sub> —2 per cent . . . . .	5.0	0.5	2.0	"	4,825	0	12	7.41
13. MgSO <sub>4</sub> —2 per cent, straw—5 T. . .	5.0	0.5	2.0	"	4,740	0	12	7.41
14. MgSO <sub>4</sub> —2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	5.0	0.6	2.0	"	4,580	0	12	7.41

\* Tons per 2,000,000 pounds soil.

The data for chlorides indicate an approximately 90 per cent recovery from added sodium chloride. Virtually all the sulfur added as sodium sulfate was recovered, and the magnesium sulfate yielded 90 per cent. This is greater recovery than that reported for a comparable period of time by Neidig and Magnuson (13) for smaller additions to Boise silt loam.

Sulfate concentration was not influenced by any treatment except sulfate additions. The otherwise general accumulation of about 30 p.p.m. of sulfur as sulfate during the incubation period indicates a normal sulfur-oxidizing

activity, even in the presence of added carbonate and chloride. The substrate originated apparently entirely from the native organic matter, decomposition of the added straw rendering inappreciable amounts of sulfur available to the sulfur-oxidizing microflora.

Microorganisms, particularly molds, were strikingly influenced by the different salt treatments, as may be seen from table 3. Total numbers in almost every case are lower than in the original sample at the beginning of the ex-

TABLE 3  
*Effect of treatments on microbial population in Willamette silty clay loam*  
After 164 days' incubation

TREATMENT	MOLDS				BACTERIA AND ACTINO-MYCES		
	Total	Mucors	Peni-cillia	Asper-gilli	Total	Actino-mycetes	Azoto-bacter*
	thous- ands	per cent	per cent	per cent	millions	per cent	
Original sample . . . . .	121	2.2	88	0	5.9	42	XX
0. No treatment . . . . .	136	0.4	61	0.2	2.1	14	X
1. Straw—5 T.† . . . . .	57	0.3	60	0.5	2.5	8	X
2. Straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	80	1.2	90	0.3	1.9	11	O
3. Na <sub>2</sub> CO <sub>3</sub> —2 per cent . . . . .	7	0	13	11.0	1.1	18	O
4. Na <sub>2</sub> CO <sub>3</sub> —2 per cent, straw—5 T. . . . .	2	0	17	16.6	1.4	21	O
5. Na <sub>2</sub> CO <sub>3</sub> —2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	18	0	14	2.9	1.2	33	O
6. NaCl—2 per cent . . . . .	103	0	88	11.6	2.9	10	O
7. NaCl—2 per cent, straw—5 T. . . . .	92	0	45	9.0	2.1	5	O
8. NaCl—2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	225	0	40	3.8	4.9	6	O
9. Na <sub>2</sub> SO <sub>4</sub> —2 per cent . . . . .	16	0	50	4.8	3.3	6	M
10. Na <sub>2</sub> SO <sub>4</sub> —2 per cent, straw—5 T. . . . .	47	0	43	1.0	3.6	8	M
11. Na <sub>2</sub> SO <sub>4</sub> —2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	23	0	88	1.1	4.7	2	M
12. MgSO <sub>4</sub> —2 per cent . . . . .	52	0	90	0.5	1.8	11	X
13. MgSO <sub>4</sub> —2 per cent, straw—5 T. . . . .	48	0	52	0	1.5	20	X
14. MgSO <sub>4</sub> —2 per cent, straw—5 T., NaNO <sub>3</sub> —125 p.p.m. . . . .	130	0	64	0	1.9	11	X

\* O = no development, X = moderate development, XX = heavy development, M = moldy.

† Tons per 2,000,000 pounds soil.

periment. This is to be expected, since during more than 5 months' incubation the various treatments had opportunity to react, and the microbial activities would probably decline to a lower state of relative equilibrium in all cases by the end of the period. The reduction in numbers of molds and bacteria by sodium carbonate, however, is outstanding; sodium sulfate had a less marked effect. Magnesium sulfate depressed bacteria more than molds. The chloride had essentially no depressing effect on molds, but, in absence of



added nitrate, considerably reduced the bacterial count. In most cases sodium nitrate greatly lessened the depressive action of the various salts.

Differentiation of the molds reveals that all salt treatments eliminated the *Mucors*; *Penicillia*, on the other hand, were little affected except by the carbonate, which was strongly depressive for this group. In contrast, the *Aspergilli* were markedly stimulated by sodium carbonate and sodium chloride; sodium sulfate had less influence, and magnesium sulfate virtually none.

The proportion of actinomyces was not greatly influenced, except for a material reduction in the presence of sodium chloride and sodium sulfate. *Azotobacter* was suppressed by sodium carbonate and by sodium chloride. The influence of the sulfate was undeterminable because of the rapidity with which molds overgrew the plaques. Magnesium sulfate was without apparent effect.

#### STUDIES ON VALE "ALKALI" SOIL

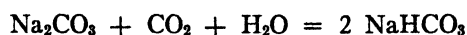
Microbial activities in a natural saline soil and in a partially reclaimed saline soil were studied in another series of experiments. These soils were obtained from the Vale Branch Experiment Station in eastern Oregon. The virgin soil is a moderately salinized heavy loam supporting semiarid desert vegetation, mainly sagebrush, greasewood, and salt grass. The reclaimed soil was taken from a plat treated with flour sulfur at the rate of 500 pounds an acre in 1932. This plat yielded 5,000 pounds of alfalfa hay in 1935, whereas check plats with corresponding irrigation yielded less than 100 pounds. Bulk samples were taken in April, 1936. Chemical properties of these samples are given in table 4.

Portions of each soil were treated with various materials as indicated in table 5, and water was added to give 60 per cent saturation. These samples were incubated in the respiration apparatus for 215 days at room temperature and sampled at 115 days and at 215 days for chemical analysis and microbial counts.

Effect of the various treatments on carbon dioxide production is shown in figures 2 and 3, the check being taken as zero. The results with the two soils were similar. Only with glucose did the reclaimed soil give a significant increase over the virgin soil. In general, the trend of carbon dioxide formation as affected by various treatments in the two soils is in the same order. In the virgin soil 1 ton of sulfur had a slight depressing effect, and 2 tons gave a slight increase; ammonium sulfate exerted essentially no influence. On the other hand, in the reclaimed soil 2 tons of sulfur caused depression, and 1 ton gave a slight increase; ammonium sulfate, again, had little effect.

The sulfur additions had a depressing influence on evolution of carbon dioxide from straw, the effect being most pronounced in the virgin soil. Nitrate was slightly depressive in the virgin soil, but gave reverse results in the reclaimed soil.

It is evident that carbon dioxide evolution carries additional significance for carbonate-bearing soils as compared with noncarbonate-bearing soils, since carbon dioxide liberated in decomposition of organic matter will react according to the following equation:



Apparent carbon dioxide evolution is reduced in proportion to bicarbonate formed. Furthermore, carbonates may be decomposed by the various in-

TABLE 4

*Chemical properties of virgin and reclaimed "alkali" soils from Vale experimental plats*  
(Surface 5 inches)

	VIRGIN	RECLAIMED
Moisture content of bulk sample (per cent) . . . . .	17.6	30.3
Water capacity (per cent) . . . . .	57.0	80.7
pH . . . . .	9.82	8.75
Total nitrogen (per cent) . . . . .	0.054	0.123
Organic matter (per cent) . . . . .	1.31	1.84
<i>Water-soluble salts:</i>		
Total (p.p.m.) . . . . .	3,150	1,310
CO <sub>3</sub> (p.p.m.) . . . . .	1,019	0
HCO <sub>3</sub> (p.p.m.) . . . . .	0	330
S as SO <sub>4</sub> (p.p.m.) . . . . .	79	30
P as PO <sub>4</sub> (p.p.m.) . . . . .	0.1	1.5
Cl (p.p.m.) . . . . .	108	76
Na (p.p.m.) . . . . .	1,200	969
Ca (p.p.m.) . . . . .	76	125
<i>Replaceable Bases:</i>		
Exchange capacity (equiv. p.p.m.*) . . . . .	242	129
Ca and Mg (equiv. p.p.m.) . . . . .	25	98
Na (equiv. p.p.m.) . . . . .	203	27
K (equiv. p.p.m.) . . . . .	15	4
Ca as per cent of exchange capacity . . . . .	10.2	75.2
Na as per cent of exchange capacity . . . . .	83.8	21.0

\* Equivalent p.p.m. = p.p.m.  $\times \frac{1}{\text{equivalent weight}}$ .

For discussion of this method of expression, see Bollen and Neidig, *Soil Sci.*, 24: 69-70 (1927).

organic and organic acids of microbial origin, thus giving rise to apparent increase in soil respiration. These various carbon transformations are well illustrated in table 9.

Table 5 indicates the change in mineral and biological carbon in virgin saline soil as affected by the treatments. The shift in mineral carbon shows a strong biological pressure effect; from 70 to 85 per cent of the total biological

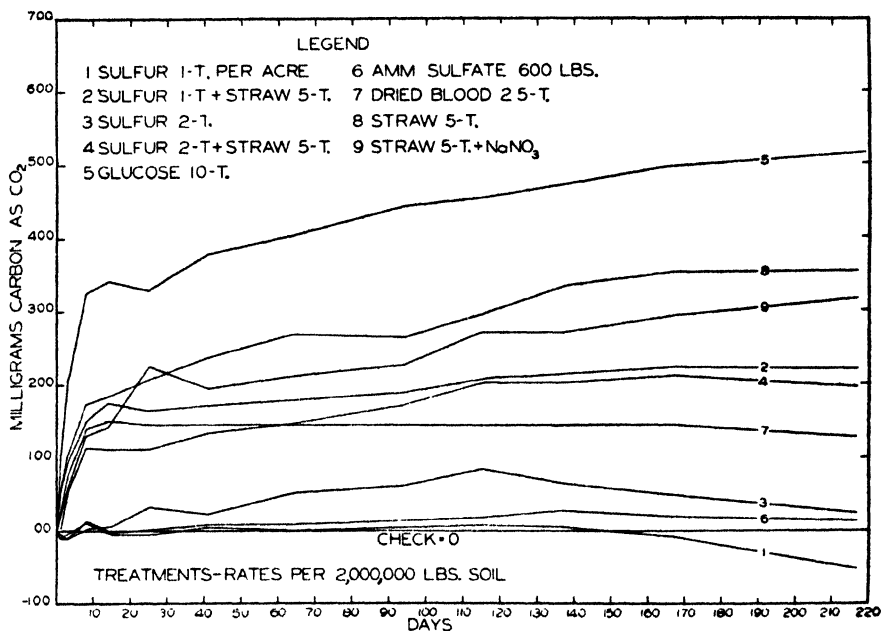


FIG. 2. EFFECT OF TREATMENT ON CARBON DIOXIDE EVOLVED FROM VIRGIN SALINE SOIL

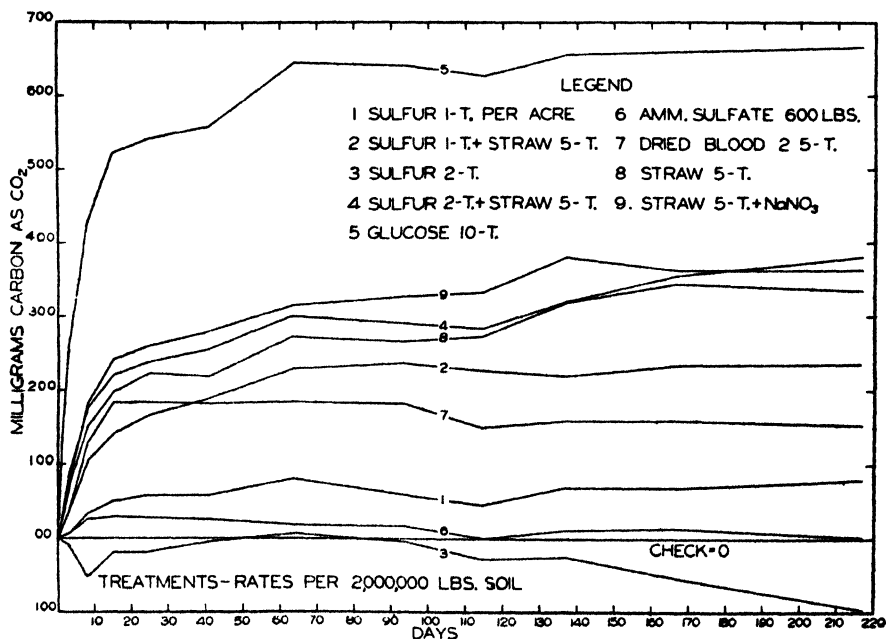


FIG. 3. EFFECT OF TREATMENT ON CARBON DIOXIDE EVOLVED FROM RECLAIMED SALINE SOIL

TABLE 5  
*Effect of treatments on change in mineral and biological carbon with time in virgin saline soil from Vale Experiment Station*

TREATMENT	MINERAL CARBON						TOTAL CARBON EVOLVED AS CO <sub>2</sub> †	BIOLOGICAL CARBON EVOLVED AS CO <sub>2</sub> ‡			
	CO <sub>2</sub>		HCO <sub>3</sub>		Total						
	Incubation period, days										
	115	215	115	215	115	215					
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.			
0. No treatment.....	120	100	14	80	134	180	675	930	605	906	
1. Sulfur-1 T. §.....	24	0	123	67	147	67	57	682	878	625	741
2. Sulfur-1 T., straw-5 T. ....	36	0	121	61	157	61	47	881	1,150	834	1,007
3. Sulfur-2 T. ....	36	0	141	61	177	61	27	759	953	732	810
4. Sulfur-2 T., straw-5 T. ....	12	0	141	61	153	61	51	877	1,125	826	1,082
5. Glucose-1 per cent. ....	108	60	61	92	169	152	35	1,130	1,444	1,095	1,392
6. (NH <sub>4</sub> )SO <sub>4</sub> -300 p.p.m. ....	60	60	122	88	182	148	22	692	943	670	887
7. Dried blood-2,500 p.p.m. ....	60	24	82	85	142	109	62	819	1,058	757	963
8. Straw-5 T. ....	60	90	102	82	162	172	42	970	1,281	928	1,249
9. Straw-5 T., NaNO <sub>3</sub> -125 p.p.m. ....	60	102	100	98	160	200	44	947	1,246	903	1,242
Original sample .....	204		0		204						

\* Total in original sample less total in treated portion.

† In respiration apparatus.

‡ By difference, total carbon minus mineral carbon.

§ Tons per 2,000,000 pounds soil.

carbon dioxide was produced during the first period. At the same time the carbonate-bicarbonate shift was most extensive. That carbon dioxide originating directly from microbial activity plays a considerable part in this shift is shown by results obtained with the untreated soil as well as with glucose and straw treatments. Additions which gave rise to an abundance of mineral acids produced, during the first half of the experiment, the greatest concentrations of bicarbonate; subsequently they also contributed to the most rapid bicarbonate decomposition. Although microbial activity decreased in the final period, carbon dioxide tension in the untreated soil was sufficient to increase bicarbonate from 14 to 80 p.p.m., more biological carbon dioxide being absorbed and converted to mineral combination. This absorption is accounted for only in part by the 20 p.p.m. decrease in normal carbonate. The remaining 46 p.p.m. must have been absorbed by bases from the exchange complex.

A greater conversion of biological carbon to bicarbonate occurred with the glucose treatment. Approximately 40 per cent more carbon dioxide was produced than in the untreated soil, and mineral absorption was much greater, especially during the first 115 days. This can be attributed to the ease with which glucose is fermented, resulting in an early rapid activity and high microbial pressure, which correspondingly increased carbon dioxide concentration in the soil. Action of organic acids is reflected by the materially lowered pH.

Carbonate was decreased approximately 85 per cent by all sulfur treatments in the first period. At the close of the experiment 70 per cent of the carbonate carbon had been evolved as carbon dioxide, and 30 per cent remained as bicarbonate. Although the larger application of sulfur was much more effective than the smaller application in lowering pH, the effect on carbonate was little different. Addition of straw with sulfur caused additional lowering of pH, probably because of buffering properties of organic decomposition products as well as of increased carbon dioxide production. Here again the carbonate relations were not appreciably altered. The course of sulfur oxidation is indicated both by increase in sulfate and by decrease in pH (table 9).

A comparison of straw alone with straw plus sulfur indicates that sulfur retarded decomposition in the virgin saline soil (fig. 2 and table 9). This may well be because the decomposing microorganisms require a relatively long period to become acclimated to a lower pH. There is similar evidence that acclimatization is incomplete in the reclaimed soil.

Table 7 shows that in the reclaimed soil the changes in mineral and biological carbon were similar to those of virgin soil. The only difference is the absence of normal carbonate in the reclaimed soil, mineral carbon being present entirely in the form of bicarbonate. Only metabolic acids other than carbonic can alter soil bicarbonates, and here again the microbial pressure was more effective during the first period than during the second period.

The application of various materials to the virgin soil resulted in an increase in the number of bacteria and molds, as indicated in table 6. Slight reduction occurred in the number of actinomycetes. With few exceptions, the results show that the microorganisms tend to decrease in the second period. The contrary is true for *Azotobacter*, which showed no development in the first period and moderate to heavy development in the second period. In general, the various treatments were effective in increasing the numbers of microorganisms. Similar results obtained in the reclaimed soil (table 8), with the exception that in most cases moderate development of *Azotobacter* occurred

TABLE 6

*Effect of treatments on microbial population in virgin saline soil from Vale Experiment Station*

TREATMENT	BACTERIA*		ACTINOMYCES*		MOLDS†		AZOTOBACTER‡	
	Incubation period, days							
	115	211	115	211	115	215	115	211
0. No treatment . . . . .	2.0	1.9	0.6	0.3	20	22	O	X
1. Sulfur—1 T.§ . . . . .	2.2	2.9	0.3	0.1	29	25	O	X
2. Sulfur—1 T, straw—5 T. . . . .	3.5	3.9	0.3	0.1	33	30	O	X
3. Sulfur—2 T. . . . .	5.5	5.7	0.2	0.1	33	29	O	X
4. Sulfur—2 T., straw—5 T. . . . .	7.0	6.8	0.3	0.1	24	20	O	X
5. Glucose—1 per cent . . . . .	4.0	3.5	0.5	0.2	29	52	O	X
6 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> —300 p.p.m. . . . .	2.8	3.2	0.1	0.1	25	23	O	XX
7. Dried blood—2,500 p.p.m. . . . .	3.8	1.9	0.7	0.2	23	24	O	XX
8 Straw—5 T. . . . .	3.0	2.0	0.1	0.1	20	21	O	XX
9. Straw—5 T., NaNO <sub>3</sub> —125 p.p.m . . . . .	2.7	1.9	0.2	0.1	23	20	O	X
Original sample . . . . .	1.4		0.2		10		O	O

\* Millions.

† Thousands.

‡ O = no development, X = moderate development, XX = heavy development.

§ Tons per 2,000,000 pounds soil.

in the second period as compared to the heavy development in the first period. This may have been due in part to the change in reaction.

The response of virgin and reclaimed soil to the various treatments is shown in table 9. Comparison of the data reveals that on the basis of biological carbon dioxide evolution the two soils respond essentially alike in all cases. All treatments had a marked effect in lowering the carbonate content of virgin samples; sulfur, the most effective treatment, completely eliminated normal carbonate by the close of the experiment. With the decrease in normal carbonate, bicarbonate increased and pH decreased. On the other hand, in the reclaimed soil, bicarbonate decreased, since no normal carbonate was present. The decrease was most pronounced with the sulfur treatments.

TABLE 7  
*Effect of treatments on change in mineral and biological carbon with time in reclaimed saline soil from Vale Experiment Station*

TREATMENT	MINERAL CARBON						MINERAL CARBON EVOLVED AS CO <sub>2</sub> *	TOTAL CARBON EVOLVED AS CO <sub>2</sub> †	BIOLOGICAL CARBON EVOLVED AS CO <sub>2</sub> ‡			
	CO <sub>2</sub>		HCO <sub>3</sub>		Total							
	115	215	115	215	115	215						
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.						
0. No treatment. ....	0	0	41	40	41	40	25	26	644	901	619	875
1. Sulfur-1 T. §.....	0	0	41	31	41	31	25	35	690	983	665	948
2. Sulfur-1 T., straw-5 T.....	0	0	41	24	41	24	25	42	872	1,138	847	1,096
3. Sulfur-2 T.....	0	0	41	18	41	18	25	48	615	804	590	756
4. Sulfur-2 T., straw-5 T.....	0	0	41	18	41	18	25	48	928	1,283	903	1,235
5. Glucose-1 per cent.....	0	0	53	24	53	24	13	42	1,271	1,568	1,258	1,526
6. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> -300 p.p.m.....	0	0	41	33	41	33	25	33	644	902	619	869
7. Dried blood-2,500 p.p.m.....	0	0	41	34	41	34	25	32	795	1,054	770	1,022
8. Straw-5 T.....	0	0	53	31	53	31	13	35	918	1,236	905	1,201
9. Straw-5 T., NaNO <sub>3</sub> -250 p.p.m.....	0	0	53	31	53	31	13	35	977	1,264	964	1,229
Original sample .....	0						66					

\* Total in original sample less total in treated portion.

† In respiration apparatus.

‡ By difference, total carbon minus mineral carbon.

§ Tons per 2,000,000 pounds soil.

There was a significant difference in the sulfur-oxidizing power of the soils. At the close of the experiments, 100 per cent of the sulfur added to the reclaimed soil was oxidized, and only 20 to 30 per cent of the sulfur was oxidized in the virgin soil. Sulfur oxidation in both soils was more extensive in the first period than in the second period. No change in sulfates occurred with other treatments, except where actual addition was made, as in the ammonium sulfate treatment. All treatments increased the amount of water-soluble phosphorus, sulfur being the most effective.

Nitrates were more abundant in the reclaimed soil than in the virgin soil under all treatments except dried blood, which was more completely nitrified

TABLE 8

*Effect of treatments on microbial population in reclaimed saline soil from Vale Experiment Station*

TREATMENT	BACTERIA*		ACTINOMYCES*		MOLDS†		AZOTOBACTER‡	
	Incubation period, days							
	115	215	115	215	115	215	115	215
0. No treatment . . . . .	5.0	4.8	0.7	0.5	20	23	X	X
1. Sulfur—1 T.‡	6.4	5.2	0.5	0.4	28	33	X	X
2. Sulfur—1 T., straw—5 T. . . . .	5.7	5.9	0.6	0.6	20	15	XX	X
3. Sulfur—2 T. . . . .	5.6	6.0	0.6	0.5	19	14	XX	X
4. Sulfur—2 T., straw—5 T. . . . .	5.6	5.5	0.5	0.3	24	27	XX	X
5. Glucose—1 per cent . . . . .	5.4	5.6	0.6	0.7	22	26	X	X
6. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> —300 p.p.m. . . . .	5.4	4.6	0.6	0.4	28	26	X	X
7. Dried blood—2,500 p.p.m. . . . .	6.8	5.1	0.4	0.2	21	17	X	XX
8. Straw—5 T. . . . .	5.4	5.2	0.4	0.4	30	24	XX	XX
9. NaNO <sub>3</sub> —125 p.p.m. . . . .	5.4	5.2	0.4	0.5	21	25	XX	XX
Original sample. . . . .	4.6		0.5		9		X	

\* Millions.

† Thousands.

‡ X = moderate development, XX = heavy development.

§ Tons per 2,000,000 pounds soil.

in the virgin soil. This better nitrification may have been due to the presence of normal carbonate, for it has been shown (2, 11) that sodium carbonate increases ammonification of dried blood. Where straw was added, nitrates decreased in the reclaimed but not in the virgin soil; there were no significant changes in carbon dioxide evolution to correlate with this. Ammonium sulfate was more completely nitrified in reclaimed soil. Because carbonates are a source of carbon dioxide in the presence of mineral acids, decrease in nitrification and sulfur oxidation, as well as lowered microbial activities in general, contributed to the decreased carbon dioxide evolution during the second period.



TABLE 9  
Comparative response of virgin and reclaimed saline soils to sulfur and organic treatments

TREATMENT	INCUBATION PERIOD	CARBON EVOLVED AS CO <sub>2</sub>				WATER-SOLUBLE SALTS												pH	
		Biological		Mineral		CO <sub>2</sub>		HCO <sub>3</sub>		Sulfur as SO <sub>4</sub>		Phosphorus as PO <sub>4</sub>		Nitrogen as NO <sub>3</sub>					
		Virgin	Re-claimed	Virgin	Re-claimed	Virgin	Re-claimed	Virgin	Re-claimed	Virgin	Re-claimed	Virgin	Re-claimed	Virgin	Re-claimed	Virgin	Re-claimed		
		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	
Original sample.....	days	...	...	...	...	1,019	0	0	330	79	30	Tr.*	1.5	2	23	9.82	8.75		
	115	605	619	70	25	600	0	68	205	83	28	Tr.	2.5	5	25	9.63	8.66		
	215	906	875	24	26	501	0	398	198	84	29	2.0	3.1	6	30	9.76	8.63		
1. Sulfur—1 T.†.....	115	625	665	57	25	120	0	616	205	275	1,110	Tr.	2.7	8	36	9.61	8.23		
	215	741	948	137	35	0	0	336	153	398	1,250	7.5	15.7	9	45	9.26	7.60		
2. Sulfur—1 T., straw—5 T.....	115	834	847	47	25	180	0	603	205	301	1,110	Tr.	2.7	5	38	9.54	7.98		
	215	1,007	1,096	143	42	0	0	305	122	435	1,250	7.5	15.7	7	45	8.96	7.41		
3. Sulfur—2 T.....	115	732	590	27	25	180	0	704	205	427	2,500	Tr.	2.9	4	33	9.54	7.88		
	215	810	756	143	48	0	0	305	91	440	2,500	6.0	15.7	10	45	7.50	7.10		
4. Sulfur—2 T., straw—5 T.....	115	826	903	51	25	60	0	704	205	431	2,500	Tr.	2.7	0	23	8.68	7.87		
	215	1,082	1,235	143	48	0	0	305	92	490	2,520	12.5	15.7	5	23	7.20	7.30		
5. Glucose—1 per cent.....	115	1,095	1,258	35	13	540	0	303	266	75	25	Tr.	2.7	7	45	8.96	8.57		
	215	1,392	1,526	52	42	300	0	458	122	79	26	1.3	8.3	12	75	8.80	8.63		
6. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> —300 p.p.m.....	115	670	619	22	25	300	0	609	205	260	45	Tr.	2.7	30	75	9.55	8.59		
	215	887	869	56	33	300	0	442	166	256	50	1.3	12.0	50	150	9.50	8.61		

7. Dried blood—2,500 p.p.m. ....	115	757	770	62	25	300	0	409	205	83	26	Tr.	2.5	150	84	9.21	8.30
	215	963	1,022	95	32	120	0	427	169	84	25	1.3	8.5	194	156	9.20	8.28
8. Straw—5 T.....	115	928	905	42	13	300	0	510	266	83	26	Tr.	2.5	5	19	9.81	8.66
	215	1,249	1,201	32	35	450	0	412	153	84	25	1.3	4.5	8	Tr.	9.80	8.83
9. Straw—5 T, NaNO <sub>3</sub> —125 p.p.m.....	115	903	964	44	13	300	0	509	266	80	26	Tr.	2.5	10	20	9.82	8.69
	215	1,242	1,229	4	35	500	0	488	153	84	25	1.3	4.5	15	Tr.	9.81	8.74

\* Tr. = less than 0.1 p.p.m.

† Tons per 2,000,000 pounds soil.

## CONCLUSION

Notwithstanding an amount of salinity and alkalinity that is deleterious to agricultural plants, the virgin soil from the Vale Branch Experiment Station harbors an active and versatile microbial population, and the usual functions significant to soil fertility are neither lacking nor significantly restricted. Reclamation of moderately salinized soils of the Vale type can thus be regarded as desirable more from the standpoint of direct influence on crop plants than from benefits occurring indirectly through effects on soil microorganisms. The sulfur-oxidizing power of the reclaimed soil, however, is much greater than that of the virgin soil. This significant difference is to be expected from stimulation of the sulfur-oxidizing microflora by the sulfur added in reclamation. In a former investigation (9), it was found that sulfur-oxidizing efficiency in several widely different soil types had been increased by previous sulfuring.

Results obtained in the experiment with Willamette silty clay loam showed decidedly depressive effects from "alkali" salts, but these effects were obtained with concentrations much greater than those in the Vale soil.

## SUMMARY

Carbon dioxide evolution in saline soils must be corrected for mineral carbon contributed or withdrawn by carbonates before it can serve as an index of organic matter mineralization. When so corrected, it is equal in importance to ammonification, nitrification, and other specific soil microbial activities in evaluating effects of salinity on functions significant to soil fertility.

Bio-organic decomposition was studied in an artificially salinized soil and in a natural solonetz under laboratory conditions by establishing a carbon balance which accounted for changes in carbonate and bicarbonate as well as for carbon dioxide evolution.

A slightly acid soil from the subhumid Willamette Valley region was treated with various "alkali" salts and incubated in a laboratory respiration apparatus for 164 days. Determination of carbon dioxide evolution and other soil microbial activities gave the following results:

All the salts depressed the rate of decomposition of the native soil organic matter as well as that of added straw.

Sodium chloride was most depressive; sodium sulfate, least depressive; and magnesium sulfate and sodium carbonate were intermediate in effect.

Nitrate accumulation was retarded in about the same order as carbon dioxide evolution.

Sulfur oxidation was not influenced by sodium chloride or sodium carbonate.

Water-soluble phosphate was indirectly influenced, being decreased as pH was increased.

Microbial function was similarly studied in a virgin "alkali" soil and in its reclaimed counterpart. The following results were obtained:

Reclamation has had little permanent influence on the native microflora and their activities in the Vale soil. Microbial response of the virgin soil to various additions was similar to that of the reclaimed soil. The latter, however, was superior in sulfur-oxidizing capacity.

The virgin soil nitrified dried blood and decomposed straw more effectively but was less effective in nitrifying ammonium sulfate and in decomposing glucose.

Normal carbonate was completely eliminated from the virgin "alkali" soil by sulfur oxidation; 70 per cent was eliminated as carbon dioxide, and 30 per cent was transformed to bicarbonate. Oxidation of native and added organic matter, as well as nitrification, produced similar but less extensive carbonate transformation. Bicarbonates in the reclaimed soil were reduced 40 to 70 per cent by microbial activity.

A microbial pressure effect is evident in the various transformations. This is greatest during the initial period of high activity stimulated by the establishment of optimum conditions, and is especially well revealed by carbonate-bicarbonate shifts.

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# FURTHER STUDIES OF BACTERIUM GLOBIFORME AND THE INCIDENCE OF THIS TYPE OF ORGANISM IN CANADIAN SOILS<sup>1</sup>

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The interest surrounding *Bacterium globiforme* has been less concerning its functions in the soil than its presence or absence in that medium, and the peculiar morphological change exhibited by the organism in turning from a definite rod-shaped cell to a coccus form. Conn (2) during a study of the so-called punctiform-colony-forming bacteria found that a large proportion of the organisms studied showed this change in morphology. It was felt that the presence of these coccus-forming rods in soil might account for the fact that direct microscopic examination of untreated soils revealed largely coccus-like organisms. In two later papers by the same author (13, 3) the ability of the type species, *Bact. globiforme* Conn, to grow in inoculated sterilized soils was tested. Two soils, Volusia silt loam and Hoosick course sandy loam, were found to be incapable of supporting growth of the organism. Both soils were highly acid, but it was found necessary to supply suitable nitrogen and carbon sources in addition to lime in order to produce growth of *Bact. globiforme*. The conclusion was drawn that although a soil supporting good growth of this microorganism does not necessarily possess a high crop-producing power, crops cannot thrive in a soil deficient in the substances required for the nutrition of the organism.

Further work was carried out by Conn and Darrow (5) on the same two soils. Growth tests were made on inoculated sterilized samples treated with organic and inorganic nitrogen sources and also with salts of the strong alkali metals. Results indicated that ammonium salts, nitrates, certain forms of organic nitrogen, hydroxides, sulphates, carbonates, and phosphates could promote growth of *Bact. globiforme*. The authors concluded that the two soils under investigation, although high in total nitrogen, lacked available nitrogen, and hence growth of *Bact. globiforme* could be obtained by addition of available nitrogen sources, or by conversion of the unavailable to available nitrogen by means of certain salts of alkali metals.

Conn (3) and Conn and Darrow (6) attempted to measure the utilization of glucose by *Bact. globiforme*. In preliminary experiments using a synthetic medium plus 1 per cent glucose it was found that 7 to 83 per cent of the sugar was utilized. Such a variation in consumption was attributed to the fact that as the

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organism did not grow normally on agar, conditions for growth in liquid media would be still more abnormal. Later experiments showed that the highest percentage of glucose was utilized when the initial concentration was approximately 0.2 per cent. It was estimated that between 48 and 75 per cent of the carbohydrate was utilized and that 50 to 60 per cent of the carbon in that fraction was converted into  $\text{CO}_2$ .

A study of the utilization of nitrogen from 0.1 per cent ammonium phosphate showed that 60 to 90 per cent of the nitrogen furnished was consumed and that 70 to 80 per cent of that consumed was converted into cell substance.

The general conclusions reached by Conn and Darrow in their most recent work (6) on *Bact. globiforme*, which summarize most of their previous work, are worthy of note. The authors conclude that *Bact. globiforme* retains in the soil, nitrogen that has been converted by other microorganisms into a soluble form and which otherwise would have been removed by drainage or utilized by plants. Whether the action is harmful on account of competition of the organism for nitrate nitrogen, or whether it may be a beneficial action in prevention of loss of nitrogen by leaching is problematical. In view of the fact that *Bact. globiforme* is ordinarily more abundant in better soils, the beneficial action probably predominates. The organism is strictly aerobic and is well adapted to surface soil conditions, where, utilizing simple sources of nitrogen and very small quantities of carbohydrate, it converts inorganic material into cell substance which is readily converted into humus upon the death of the organism.

Taylor and Lochhead (11) determined numbers of *Bact. globiforme* in field plots and found the organism to be as prevalent in a soil of low fertility, cropped continuously for 25 years without application of fertilizer, as in plots of much greater crop-producing power to which farmyard or artificial manures had been applied. It was also observed that the metamorphosis from rod to coccus was not merely a shortening of the rod until the organism became spherical, but a swelling of the rod followed by a fragmentation, leaving ovoid bodies which became cocci.

More recently Topping (15), in an investigation of the predominant microorganisms in soils, found coccus-forming rods to be the most common type. These were divided into three groups:

- Group 1. Gram-positive, motile bacteria which may produce branching variants.
- Group 2a. Gram-positive, nonmotile, rod-shaped bacteria.
- Group 2b. Gram-positive, nonmotile, mycelium-forming bacteria.

Relationship of *Bact. globiforme* Conn to group 2a is suggested by the author on the basis of the nonmotility of the organism and the fact that no branched forms had been noticed. Taylor and Lochhead (12), however, have since observed branched forms in cultures of *Bact. globiforme* Conn, and suggest that all three of Topping's groups contain strains of the *Bact. globiforme* group of organisms. Such a suggestion is strengthened by a comparison of photographs obtained by the respective authors.

In a previous paper (11) from this laboratory it was suggested that the inability to determine greater numbers of *Bact. globiforme* in soils of high crop-producing power than in a plot of low crop-producing power might be due to the fact that the latter soil had been rendered infertile by continuous cropping and hence was not strictly comparable with the naturally infertile soils with which Conn worked. To test this point it was decided to examine a large number of soils of different types and fertilities for the presence and abundance of *Bact. globiforme*.

#### MATERIAL AND METHODS

Through the coöperation of the Branch Farms and Stations of the Experimental Farms System, soil samples were obtained from widely scattered districts extending from as far east as Kentville, Nova Scotia, west to Saanichton, Vancouver Island, and as far north as Beaverlodge, Alberta, and Fort Good Hope, Northwest Territories.

The samples were typical of a large variety of different soils, from both the pedological and the agricultural aspects, and were representative of virgin, prairie, orchard, garden, pasture, and mixed cropped soils. Two or more samples, usually of different crop-producing power, were received from each district. Because of the time elapsing between the receipt of the soils and their sampling, it was thought best for comparative purposes to allow the samples to air dry at room temperature before examination.

The soils were plated on tap-water gelatin medium, and the plates were incubated 7 days at 18°C. A dilution of 100,000 was employed but in some instances proved to be excessive, hence replating at a lower dilution was necessary. Bacterial colonies appearing on the plates were counted, and from a sector of each plate 20 colonies were picked off and inoculated on nutrient agar slopes. After 5 days' incubation at 28°C. the subcultures were examined by means of preparations stained with gentian violet. Most of the organisms of the *Bact. globiforme* type were readily identified by their coccus form, but in many instances the organisms still appeared as rods and prolonged incubation was necessary for confirmation. With experience *Bact. globiforme* could be differentiated from true cocci; where any doubt existed as to a culture's being one or the other, subcultures were made and examined after 24 hours' incubation.

The pH values of the various soil samples were measured electrometrically by the quinhydrone electrode.

#### EXPERIMENTAL

Of 90 soils examined, *Bact. globiforme* was isolated from 89. Table 1 shows the approximate numbers of *Bact. globiforme* present in soils of different fertility and fertilizer treatment. It can be seen that, in general, numbers tend to be higher in the more fertile plots, although Lacombe soils are a notable exception. From the figures representing numbers as a percentage of the total



plate count, it would appear that higher numbers mean not necessarily a greater relative number of *Bact. globiforme* but a greater general population.

TABLE 1  
*Numbers of Bact. globiforme in soils of different fertility supporting rotational crops*

LOCATION	TREATMENT*	FERTILITY	pH	BACT. GLOBIFORME	
				Count (100,-000)	Per cent of plate count
Charlottetown, P. E. I.	A. + F.Y.M.	.....	5.6	5.5	43.0
	A.	.....	4.8	0.14	4.6
Lennoxville, Que.	A. + F.Y.M.	Medium	6.3	22.0	55.0
	A. + F.Y.M.	Low	5.3	13.0	51.0
Ste. Anne de la Pocatière, Que.	A. + F.Y.M.	High	6.6	35.0	45.0
	A. + F.Y.M.	.....	6.8	56.0	70.0
Cap Rouge, Que.	F.Y.M.	High	6.3	188.0	94.0
	A. + F.Y.M.	Low	4.5	4.2	37.0
Kapusksasing, Ont.	F.Y.M.	.....	7.7	129.0	86.0
	None	.....	7.8	95.0	95.0
Brandon, Man.	None	High	7.6	12.0	57.0
	None	(Wind-blown)	8.5	5.4	67.0
Indian Head, Sask.	None	High	8.3	51.0	100.0
	None	High	7.8	15.0	88.0
Scott, Sask.	None	.....	7.4	8.0	61.0
	None	.....	5.9	18.0	75.0
Swift Current, Sask.	None	Good	8.3	51.0	74.0
Lacombe, Alta.	None	High	6.5	10.0	50.0
	None	Low	6.2	54.0	88.0
Lethbridge, Alta.	A. + F.Y.M.	High	8.1	142.0	94.0
	A. + F.Y.M.	P <sub>2</sub> O <sub>5</sub> -deficient	8.0	85.0	85.0
Summerland, B. C.	F.Y.M.	Medium	8.5	36.0	70.0
	F.Y.M.	Lower	8.5	37.0	77.0
Fort Good Hope, N.W.T.	.....	.....		144.0	41.0

\* A. = Artificial fertilizer; F.Y.M. = Farmyard manure.

In two soils, however, from Charlottetown, Prince Edward Island, and from Cap Rouge, Quebec, the pH values of which were lower than 5.0, it is evident

that *Bact. globiforme* is not only actually restricted but also represents a noticeably smaller percentage of the total plate count.

The effects of lime and fertilizer treatments are demonstrated in table 2. In one case, at Kentville, Nova Scotia, a series of plots cropped with a rotation of roots, grain, and clover since 1914 has been used to compare nitrate of soda with sulfate of ammonia, in each instance with and without lime. It can be seen that numbers of *Bact. globiforme* are increased enormously by the addition of lime and very slightly by the application of fertilizer. Not only were

TABLE 2  
*Effect of soil treatment on numbers of Bact. globiforme*

ROTATION	FERTILIZER	AMEND- MENT	pH	FERTILITY	BACT. GLOBIFORME	
					Count (100,- 000)	Per cent of plate count
Experimental Station, Kentville, Nova Scotia						
Roots, grain, clover	Nitrate of soda, super- phosphate, basic slag, muriate of potash	None	5.6	. . . . .	1.4	28
		Lime	6.5	....	18	60
Roots, grain, clover	Sulfate of ammonia, su- perphosphate	None	5.5	.....	0.46	15
		Lime	6.3	. . . . .	19	63
Roots, grain, clover	None	None	5.5	.....	1.4	45
		Lime	6.5	.....	12	60
Experimental Farm, Nappan, Nova Scotia						
Oats, hay	Nitrate of soda, basic slag None	Lime	7.2	Medium	23	62
		Lime	6.1	Low	10	66
Swedes, oats, hay	Farmyard manure None	Lime	6.5	High	33	70
		Lime	5.8	Low	9	64
Oats, hay	Basic slag None	None	5.3	High	16	64
		None	5.0	Medium	10	55

the numbers increased by lime but also the proportion of the total plate count was materially increased, suggesting a group stimulation. In the other instance, figures are shown for fertilized and check plots from three rotational systems in operation since 1923 at Nappan, Nova Scotia. In all three cases numbers show a substantial increase with fertilizer treatment, most particularly so with farmyard manure. Increases are all proportional to the increase in the total plate count, and hence *Bact. globiforme* was not preferentially stimulated. The plot system did not permit deduction as to the effect of lime.

Table 3 includes a number of miscellaneous soils, such as garden, orchard, virgin, and Ontario tobacco soils. Apparently *Bact. globiforme* is as prevalent in virgin soils as in cultivated soils. The Swift Current sample is an exception: the *Bact. globiforme* count is very low, and a comparison with the other sample (table 1) taken from an adjoining cultivated field shows greater num-

TABLE 3  
*Numbers of Bact. globiforme in miscellaneous soils*

LOCATION	SOIL	TREATMENT*	pH	BACT. GLOBIFORM	
				Count (100,000)	1 per cent of plate count
Agassiz, B.C.	Garden	F.Y.M.	6.7	29.0	50.0
	Orchard	None	8.3	10.0	50.0
Saanichton, B.C.	Garden	F.Y.M.	7.4	37.0	80.0
	Orchard	.....	6.0	12.0	60.0
Windermere, B.C.	Garden	F.Y.M.	8.3	53.0	80.0
	Pasture	Virgin	7.6	8.0	66.0
Beaverlodge, Alta.	Woodland	Virgin	7.0	72.0	92.0
	Woodland	Virgin	6.1	29.0	28.0
Melfort, Sask.	Prairie	Virgin	6.0	63.0	84.0
Swift Current, Sask.	Prairie	Virgin	7.7	0.97	54.0
Essex County, Ontario	Orchard	.....	6.0	6.0	55.0
	Tobacco	Artificials	6.2	17.8	72.0
	Tobacco	Artificials	6.2	0.9	51.0
	Tobacco	Artificials	6.3	2.2	58.0
	Oats	F.Y.M.	7.0	3.5	40.0
	Wheat	.....	7.3	40.0	88.0
	Wheat	F.Y.M.	6.0	18.0	80.0
Kent County, Ontario	Tobacco	Artificials	6.8	26.0	86.0
	Tobacco	Artificials	6.8	13.0	68.0
Parry Sound, Ontario	Oats	.....	6.0	0.0	0.0

\* F.Y.M. = Farmyard manure.

bers in the cultivated soil. The Ontario soils had been collected and air dried several months before they were received at the laboratory, but relatively large numbers of *Bact. globiforme* were isolated from them in most instances. *Bact. globiforme* was not found in the Parry Sound sample, but this is believed to be due to inability to isolate the organism rather than to its absence. The gelatin plate count of this soil is only 200,000 per gram. Lowering the dilu-

tion sufficiently to allow the growth of 15 to 20 colonies results in the appearance of gelatin-liquefiers, which liquefy the medium before any slow growers can make an appearance.

#### DISCUSSION

The assertion of Conn (3) that general crops cannot thrive in a soil deficient in the substances required for the nutrition of *Bact. globiforme* may be correct, but the fact that from only one sample of soil, a soil that was air dried for several months, was *Bact. globiforme* not isolated, suggests that it is difficult to obtain such soils to test the theory. The results of this investigation show that, from a geographical standpoint, the organism is as abundant in a soil situated on the rim of the Arctic Circle as in soils on the Atlantic and Pacific coasts of southern Canada. It is present in garden, prairie, orchard, marsh, and mixed cropped soils, whether acid, neutral, or alkaline, fertile or infertile.

In general, counts of *Bact. globiforme* in soils do not provide any more information than can be obtained from a total plate count, but it would appear that in soils more acid than pH 5.0 this type of organism is severely repressed. This is interesting in view of the fact that the two soils in which Conn could initiate no growth of *Bact. globiforme* were as acid as pH 4.5. In point of fact, in an earlier paper (13) growth was reported when an unmeasured amount of  $\text{CaCO}_3$  was added to the soil, but later (3) the statement was modified to the effect that the organism was virtually unable to grow. In the latter work the enormous dosage of 1 per cent  $\text{CaCO}_3$  was employed. In view of the wide range of carbon and nitrogen sources that *Bact. globiforme* Conn is capable of utilizing, it is difficult to ascribe any reason, other than acidity or the presence of some toxic substance, for the failure of the organism to grow in soil.

#### MORPHOLOGY AND PHYSIOLOGY OF THE BACT. GLOBIFORME GROUP

In previous work (11) it was found that of the cultures isolated, many separate strains could be differentiated by their action on dextrose, by reduction or nonreduction of nitrates, and in some cases by pigmentation. Although all cultures showed the characteristic tendency to change from rod to coccus, the time taken to accomplish the metamorphosis and the cell size of the organism varied greatly between strains. The peculiar morphology of *Bact. globiforme* has lent itself to considerable speculation on the part of Conn and Darrow (6) and Topping (15) with regard to the systematic position of the organism. Although it is placed in Bergey's Manual (1) under the genus *Achromobacter*, Conn and Darrow do not accept this placing and state that the spherical form in soil suggests relationship to the cocci. In certain physiological aspects the organism resembles the *Bacteriaceae*. Topping considers that *Bact. globiforme* will eventually be included among the *corynebacteria*.

In order to understand more fully the relationship of the various strains of *Bact. globiforme*, the physiology of a large number of cultures isolated from widely different soils has been studied. All cultures were replated on beef-

peptone agar prior to the commencement of the experimental work. The morphology of a few strains has been examined in detail. Results have been compared with those of the type species of *Bact. globiforme* supplied by Dr. H. J. Conn.

### *Morphology in artificial media*

The morphology of the organism is profoundly affected by time and temperature of incubation and by the nature of the substrate. On beef-peptone agar young cultures are consistently short rods which vary considerably in length, tend to be slightly curved, and tend to produce clumps. A few cocci and clavate cells are commonly present. At temperatures above 28°C. large distended rods with bulbous extremities, which break off into cocci, are prevalent. As the culture ages the rods turn into cocci by a process which is virtually a swelling and fragmentation of the rod. This swelling is much more obvious in some strains than in others, and with the Conn strain can be seen clearly only at incubation temperatures of 30°C. or more. It also seems probable that the rod can divide into two or more cocci, after the nature of *Rhizobium*. The time taken to attain the coccus state varies considerably. With some strains the metamorphosis is almost complete in 48 hours, and with others, 12 or more days may elapse before the appearance of an appreciable number of cocci.

In 3-week-old cultures, certain morphological differentiations can be made. These depend upon the size of the cocci and upon the presence or absence of appreciable numbers of rod forms. Such distinctions do not appear to be correlated with any other type characteristic.

On solid synthetic media, young cultures invariably show rod morphology. If such carbohydrates as dextrose, mannite, and xylose are incorporated, together with certain forms of nitrogen, the cocci peculiar to old cultures are absent, and larger oval cells in which a small deeply stained spherical form is embodied, make their appearance. Stained clumps of these cells strongly resemble frog spawn. When ammonium salts are used as the sole source of nitrogen, the organism becomes very pleomorphic, and long swollen and branched rods outnumber cocci, even in old cultures.

The morphology is more extreme in liquid media. Cultures in nutrient broth are present as slightly curved rods after 12 hours' incubation, but later become swollen or branched. After 3 days the disintegration of the branched forms is apparent, the bulbous sprouts and extremities of the cell breaking off as cocci. In old cultures the organism is present as rather large cocci, together with an assortment of pleomorphic rods.

### *Morphology in soil*

In order that the morphology of the organism during its growth in soil might be compared with that on artificial media, portions of sterilized soil

were inoculated separately with four strains of *Bact. globiforme*, and glass microscope slides were inserted after the technic of Conn (4). Sets of jars were incubated at room temperature, at 28°C., and at lower outside temperatures. Slides were removed at intervals, stained, and examined. After 2 days' incubation, the organisms were rather sparse and were present as short rounded rods, with individuals having a banded appearance. The only difference between stains was that of a slight variation in cell size. After 8 days' incubation, the organisms were very dense in the soils kept at room temperature and at 28°C., and growth was abundant in the outside samples. The four strains of *Bact. globiforme* in all soils showed remarkable uniformity in morphology, all being present as slightly elongated cocci, only a small proportion of which could truly be said to be spherical enough to resemble staphylococci. In order to eliminate the effect of the glass-soil interface, large petri dishes were substituted for the jelly jars and the glass slides were omitted in a repetition of the work. Samples from these dishes, taken at daily intervals by means of a cork borer, were macerated with water, and stained smears were prepared. The results were similar to those of the previous experiment, and on no occasion could pleomorphic or branched rods be observed.

#### *Nitrogen requirements*

As a base for determining the availability of certain nitrogen sources, a synthetic semisolid medium of the following composition was prepared:

	gm.
K <sub>2</sub> HPO <sub>4</sub> .....	0.2
MgSO <sub>4</sub> .....	0.05
NaCl .....	0.05
CaCl <sub>2</sub> .....	0.025
Dextrose .....	10.0
Agar .....	3.0
Distilled water .....	1,000 ml.

To this basal medium were added separately, NaNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, yeast extract, beef extract, peptone, cystine, and urea in amounts calculated to give 0.01 per cent nitrogen. From 106 cultures of *Bact. globiforme* stab inoculations were made into tubes of the above media. Such semisolid media proved unsuitable for good comparison of growth, and results were so variable that any attempt at classification on a basis of acid production from carbohydrate was futile. Most of the cultures used the semianaerobic nature of the nitrate medium to break down the nitrate completely. Dextrose was used as a source of energy, and an acidic reaction was produced in the medium. Growth and acid production in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and cystine media varied greatly. The complex organic sources of nitrogen—yeast extract, beef extract, and peptone—proved adequate for excellent growth, but the production of an acidic reaction was not consistent with the three compounds.

For a better comparison of growth, a solid medium of the same basal composition as that of the semisolid medium was prepared. With the exception of beef extract and peptone, all previous nitrogen sources together with the amino acids, alanine, asparagin, glycine, and leucine, were employed. Slopes of the media were inoculated with the various cultures and examined after 3 and 8 days' incubation. Results showed that the cultures of *Bact. globiforme* could be divided into two types, those utilizing nitrate nitrogen, and those unable to do so. The former produced luxuriant growth, and the latter, slight or no growth on nitrate medium. Both types grew equally well with yeast extract as a source of nitrogen. Only 17 cultures of the 106 examined, including *Bact. globiforme* Conn, belonged to type I. The relative availability of the nitrogen sources was as follows:

Type I	$\left. \begin{array}{l} \text{Yeast extract} \\ \text{Asparagin} \\ \text{Glycine} \\ \text{NaNO}_3 \end{array} \right\}$	>	$\left. \begin{array}{l} \text{Leucine} \\ \text{Urea} \\ \text{Alanine} \end{array} \right\}$	>	$\left. \begin{array}{l} (\text{NH}_4)_2\text{SO}_4 \\ \text{Cystine} \end{array} \right\}$	slight growth	
Type II	Yeast extract	>	$\left. \begin{array}{l} \text{Leucine} \\ \text{Glycine} \\ \text{Asparagin} \end{array} \right\}$	poor growth	>	$\left. \begin{array}{l} (\text{NH}_4)_2\text{SO}_4 \\ \text{NaNO}_3 \\ \text{Alanine} \\ \text{Cystine} \\ \text{Urea} \end{array} \right\}$	trace or no growth

Production of acid was confined chiefly to those media in which  $(\text{NH}_4)_2\text{SO}_4$  and leucine were incorporated; this was probably due to the formation of sulfuric and leucic acids respectively. Sufficient acid may have been produced from  $(\text{NH}_4)_2\text{SO}_4$  to restrict the growth of the organisms on this medium, which would be necessary to conform with the work of Koser and Rettger (8), who showed that ammonia and amino nitrogen (including urea) are qualitatively equivalent as sources of nitrogen for bacteria. Such an explanation would seem justified, as organisms of type I grew well in Conn's ammonium phosphate-dextrose medium, whereas organisms of type II grew poorly or not at all.

Relative numbers of the two types, together with some cultural characteristics, are shown in figure 1.

#### Carbon sources

The availability of different carbon compounds for organisms of type I was readily determined by the use of a synthetic medium with  $\text{NaNO}_3$  as the nitrogen source. Preference was as follows:

$\left. \begin{array}{l} \text{Dextrose} \\ \text{Mannite} \end{array} \right\}$	>	$\left. \begin{array}{l} \text{Inulin} \\ \text{Glycerol} \\ \text{Raffinose} \\ \text{Xylose} \end{array} \right\}$	>	$\left. \begin{array}{l} \text{Lactate} \\ \text{Citrate} \\ \text{Acetate} \\ \text{Starch} \\ \text{Dextrin} \end{array} \right\}$
--	---	--	---	--

Usually the strains made very little growth where lactate, citrate, acetate, dextrin, or starch was the carbon source, but two strains of those tested made good growth. An acidic reaction was not produced from dextrose or glycerol, and the inconsistent and changeable reactions produced from other carbon sources only emphasized the futility of any attempt to classify the organisms on the basis of acid production.

The inability of organisms of type II to utilize inorganic or simple organic nitrogen sources necessitated employment of a more complex form, yeast extract, and hence an additional carbon source was present. Results from a few compounds tested indicated that dextrose and mannite were much more available sources of carbon and energy than were raffinose, xylose, or inulin.

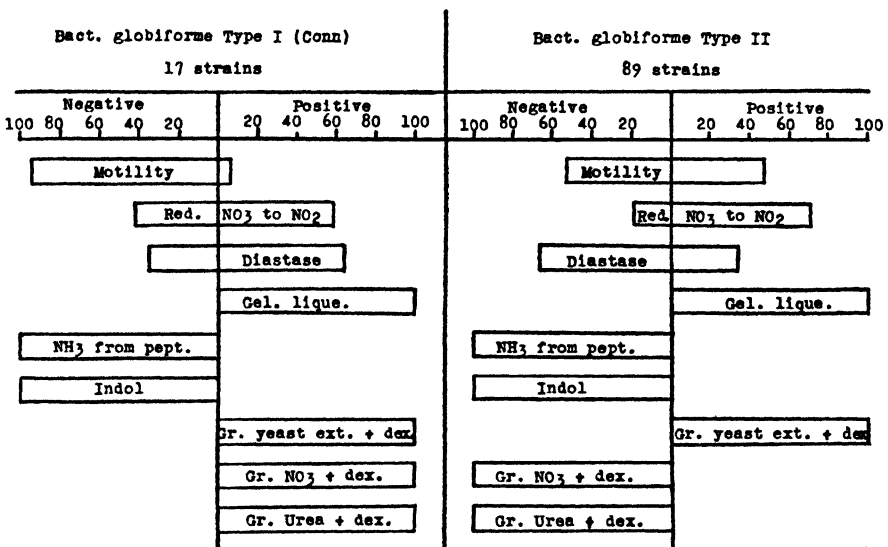


FIG. 1. CORRELATION OF CHARACTERS OF BACT. GLOBIFORME, TYPES I AND II

#### EFFECT OF ENVIRONMENT

##### Plants

Sterilized seeds of alfalfa, red clover, and timothy were sown in 8-inch by 1-inch test tubes containing a sterile nitrogen-free medium described by Thornton (14). Upon the germination of the seeds, separate tubes were inoculated with four strains of *Bact. globiforme*. No growth of the organisms was visible for the first 10 days, after which, with the aid of a magnifying glass, small bacterial colonies could be observed surrounding the rootlets of the seedlings. The colonies increased in size with time until they became visible to the naked eye and spread a considerable distance along the roots. As the plant matured, colonies became less apparent and finally disappeared. The plants showed no beneficial or harmful effects, in either root or foliage growth,



from this bacterial invasion. The attraction of *Bact. globiforme* to the roots of plants is of some interest in view of the recent work by Starkey (10), who reported that coccoid bacteria were among the most numerous types encountered in a microscopic examination of the rhizosphere.

#### *Temperature*

Strains of *Bact. globiforme*, as shown previously, can survive in soils exposed to subzero temperatures. By exposing sterilized soils which had been re-inoculated with several strains of *Bact. globiforme* to various temperatures, it was ascertained that the organisms are not so tolerant of heat as of cold. Only one culture survived an exposure to 45°C. for 24 hours, and it was killed at 50°C. These types of organisms are evidently among those eliminated by partial sterilization of the soil. The ranges of growth temperatures for various strains of *Bact. globiforme* vary considerably, and though 25°C. approximates the optimum growth temperature on nutrient agar, most strains produce some growth at 33°C. The Conn strain is the only one found to grow actively at 37°C.

#### *Acidity*

As a test of the tolerance of *Bact. globiforme* to acidity, 28 cultures were inoculated on slopes of synthetic media of various pH values. A comparison of growth was made after 5 days' incubation at 28°C., and results showed that, of the 28 cultures tested, 14 showed no growth at pH 4.0, 6 made some growth, and 8 grew well. Growth of the 14 cultures was severely repressed at pH 5.0, but all cultures grew equally well at pH 6.0, 7.0, and 8.0.

#### GENERAL CONSIDERATIONS

Outstanding characteristics of members of the *Bact. globiforme* group of organisms are their lack of uniformity in behavior, both morphological and physiological, and the strong pleomorphism influenced by the substrate. Although the change from a rod to a coccus or coccoid form invariably takes place regardless of the substrate employed, the time taken to complete such a transformation varies considerably from strain to strain. The pleomorphic rods, branched forms, and yeast-like cells which may be observed in artificial media have not been encountered in the soil and the question arises: Upon which of these forms should a morphological classification be made? Topping (15) asserts that the production of branched forms suggests relationship to the Proactinomycetaceae. Conn and Darrow (6), on the other hand, consider that the existence of *Bact. globiforme* in the soil in a coccoid form would indicate relationship to the cocci. The similarity of *Bact. globiforme* and *Rhizobium* in their utilization of dextrose, a complete oxidation resulting in cell substance and CO<sub>2</sub> only, led Conn and Darrow (6) to speculate whether *Bact. globiforme* might be related to the Bacteriaceae. Such a basis of relationship is not strengthened by the fact that Merrill (9), studying the breakdown of dextrose by the Mycobacteriaceae, was likewise unable to determine the presence of any product other than CO<sub>2</sub>. The systematic position and

relationship of coccus-forming rods, including those reported by Topping (15) and the *Mycoplana* group of Gray and Thornton (7), might well be investigated.

The 106 strains of *Bact. globiforme* studied were so diverse in such biochemical activities as the production of nitrite from nitrate, formation of diastase, and production of acidic reactions in various carbohydrate media that no two cultures proved to be identical. The ability or inability to utilize nitrate nitrogen aerobically is believed to be a better basis of separation of organisms belonging to the rod-coccus type than is the presence or absence of motility. *Bact. globiforme* Conn is representative of the former type, which is much less prevalent in the soils examined than is the latter type. Neither group has been found to be indicative of any particular type of soil.

#### SUMMARY

Of 90 soils examined, selected from widely separated points of Canada, 89 showed the presence of *Bact. globiforme*. Numbers of this organism show no relationship to fertility, but may be greater in fertile soils than in infertile soils, since fertile soils usually support a higher general bacterial population.

In virgin, prairie, garden, orchard, woodland, and mixed cropped soils, provided these soils are more alkaline than pH 5.0, *Bact. globiforme* is present in large numbers. Where application of fertilizer results in an increase in numbers of *Bact. globiforme*, the increase is not a preferential stimulation of this group but is proportional to the increase in total plate count. In soils more acid than pH 5.0 the organism is severely repressed; the application of lime to such soils increases numbers of *Bact. globiforme* in preference to other types.

The morphology of several strains of *Bact. globiforme* has been compared during growth on artificial media and in the soil. Certain pleomorphic forms observed in laboratory media have not been found to occur in soil.

The carbon and nitrogen requirements of 106 cultures of *Bact. globiforme* have been tested. Results have shown that cultures of this organism may be divided into two definite types on the basis of their nutrition, namely:

Type I. Capable of utilizing complex nitrogenous compounds, nitrate, certain amino acids, and urea as sources of nitrogen.

Type II. Capable of utilizing only complex nitrogenous compounds as sources of nitrogen.

Type II was found to be far more common in soils examined than was type I. Organisms belonging to both groups have been found to vary in respect to their biochemical reactions. When present in the soil, all show a marked resistance to low temperatures and to air drying, but are destroyed by exposure of the soils to a temperature of 45°C. for 24 hours. On artificial media more acid than pH 4.5 the majority of strains are unable to grow.

Strains of *Bact. globiforme* tested proved capable of proliferating around the roots of clover, alfalfa, and timothy seedlings growing in a sterile nitrogen-free nutrient medium.

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## PLATE 1

CULTURES OF *Bacterium globiforme* CONN

FIG. 1. *Bacterium globiforme* Conn, 12-hour culture on beef-peptone agar at 28°C., gentian violet stain, showing rod stage.  $\times 1040$ .

FIG. 2. *Bacterium globiforme* Conn, 48-hour culture on beef-peptone agar at 37°C., gentian violet stain, showing bulbous rods.  $\times 1040$ .

FIG. 3. *Bacterium globiforme* Conn, 48-hour cultures in nutrient broth at 28°C., gentian violet stain, showing branched forms.  $\times 1040$ .

FIG. 4. *Bacterium globiforme* Conn, 48-hour cultures in nutrient broth at 28°C., gentian violet stain, showing branched forms.  $\times 1040$ .

FIG. 5. *Bacterium globiforme* Conn, 2-week culture on synthetic medium containing dextrose and cystine, gentian violet stain.  $\times 1040$ .

FIG. 6. *Bacterium globiforme* Conn, 2-week cultures on synthetic medium containing dextrose and  $\text{NaNO}_3$ , gentian violet stain, showing oval yeast-like cells.  $\times 1040$ .

FIG. 7. *Bacterium globiforme* Conn, 2-week cultures on synthetic medium containing xylose and  $\text{NaNO}_3$ , gentian violet stain, showing deeply staining bodies.  $\times 1040$ .

FIG. 1



FIG. 2



FIG. 3



FIG. 4



FIG. 5



FIG. 6

FIG. 7



## OXIDATION-REDUCTION POTENTIALS IN SOILS

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The oxidation-reduction potentials ( $E_h$ ) of soils have been studied by several workers, and the literature on the subject has been summarized by Brown (1). The important findings in the fields of bacteriology, biology, and biochemistry, made possible by the use of oxidation-reduction potentials, have resulted, however, in little fundamental work on soils. The practical importance of such measurements on soils have been visualized but not realized in actual practice. Even the theoretical background is vague, and no one has demonstrated in a convincing manner the nature of the oxidant and the reductant responsible for this phenomenon, though the presence of such substances in soils could not be denied. The present paper deals chiefly with this aspect of the problem, namely, the true cause of the so-called oxidation-reduction potentials in soils.

### THEORETICAL CONSIDERATIONS

The fundamental equation involved in oxidation-reduction potentials is

$$E_h = E_o - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]}$$

where  $E_h$  is the potential in volts, referred to the normal hydrogen electrode as zero, of the system under consideration;  $E_o$  is a constant characteristic of the system and equal to  $E_h$  when the ratio  $\frac{[\text{Red}]}{[\text{Ox}]}$  is unity;  $[\text{Red}]$  and  $[\text{Ox}]$  represent the concentrations of reductant and oxidant respectively; and  $R$ ,  $T$ ,  $n$  and  $F$  have their customary significance (2, p. 367).

The equation shows  $E_h$  to be dependent on the ratio of oxidant to reductant, as well as on temperature and on the particular system under investigation. It is not generally realized that the ratio of oxidant to reductant is the most important factor in the thermodynamic relation. Wherever a definite potential difference is to be established at the electrode, there must be in the system two species, one of which is the direct or indirect reduction product of the other, and the ratio of their concentrations or activities must be of finite magnitude. Neglect of this principle is not unusual in soil literature. It must be emphasized that a system which does not reversibly maintain a finite ratio of oxidant and reductant, leaves the electrode functioning in a manner that prevents the interpretation of any results obtained. Some potential will

always be developed when a clean platinum electrode is dipped into a soil solution; but unless the thermodynamic equations can be satisfied by the introduction of known components, the results will have no fundamental value and may in fact be meaningless.

The universal presence of iron in all soil systems might reasonably be assumed and all potentials interpreted in terms of the system  $\text{Fe}^{+++} + \text{E} \rightleftharpoons \text{Fe}^{++}$ , but we cannot avoid the possibility of the participation of other systems when we are dealing with a substance like soil. The results in this case can be valuable and interpretable only if the characteristic data for one particular system can be obtained under conditions which preclude interference by another system. The relation between pH and  $E_h$  is practically linear for a system in which the ratio  $\frac{[\text{Red}]}{[\text{Ox}]}$  is constant. The relation is complex when both this ratio and pH change simultaneously, and to obtain a complete picture a figure in three dimensions is necessary. Fortunately in soils the only possible system is  $\text{Fe}^{+++}.\text{Fe}^{++}$ , which gives a constant potential for a given ratio, irrespective of the pH value. On the other hand, the range of this system is limited because at high pH values iron is precipitated. We are, therefore, confronted with a dilemma in the case of soils. The thermodynamic relation might be satisfied by the fundamental equation for the system  $\text{Fe}^{+++}.\text{Fe}^{++}$ , but the quantity of iron that can remain in solution above pH 5.0 becomes so small that the system would cease to function as such.

#### EXPERIMENTAL

In order to determine the quantity of ferrous and ferric ions that can be brought into solution from the soil, a black cotton soil of high base-exchange capacity was shaken with different buffer solutions, and ferrous iron and ferric iron were determined in the filtrate. The results are given in table 1. It will be seen that virtually no iron is brought into solution above pH 5.5, and virtually no  $\text{Fe}^{+++}$  above pH 5.0. The  $\text{Fe}^{+++}.\text{Fe}^{++}$  system, therefore, is operative only up to pH 5.0. As this pH range is scarcely ever found in natural soils, we are forced to the conclusion that this system plays no part in determining the oxidation-reduction potentials in natural soils. It is doubtful, therefore, whether any measurements of  $E_h$  on agricultural soils with the object of correlating soil behavior in the field are likely to be fruitful.

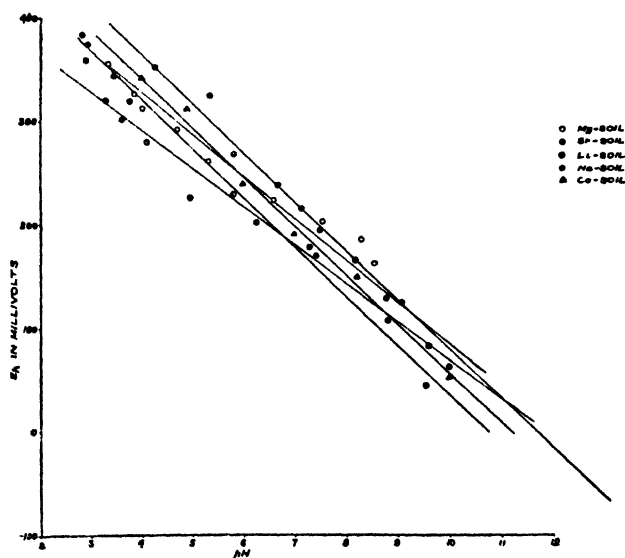
It is of interest, however, to see whether as a result of eliminating extraneous influences, the exchange complex in soils would exhibit oxidation-reduction potentials which could be interpreted in terms of some known system. It is obviously impossible to study the influence of varying  $\frac{[\text{Red}]}{[\text{Ox}]}$  ratios at constant pH in soils because we do not know even the nature of these ratios. There is, however, a possibility that under ordinary circumstances this ratio for a particular soil might be constant, in which case a study of the relation between pH

and  $E_h$  would be helpful in throwing light on the nature of this phenomenon in soils.

TABLE 1

*Ferric and ferrous iron, in grams per 100 gm. of soil, brought into solution at different pH values*

pH	FERRIC IRON	FERROUS IRON	TOTAL IRON
	gm.	gm.	gm.
0.65	0.1333	0.1167	0.2500
0.91	0.1046	0.1069	0.2115
1.42	0.0602	0.0939	0.1541
1.85	0.0256	0.0898	0.1154
2.32	0.0208	0.0753	0.0961
2.64	0.0132	0.0584	0.0716
3.09	0.0033	0.0341	0.0374
3.61	0.0064	0.0255	0.0319
3.95	0.0054	0.0234	0.0288
4.39	0.0040	0.0204	0.0244
4.76	0.0026	0.0170	0.0196
5.20	0.000067	0.0100	0.0101
5.50	0.000000	.....	.....

FIG. 1. RELATION BETWEEN pH AND  $E_h$  OF SINGLE-BASE SOILS

Soils used for this study were treated with 0.05 *N* HCl to remove all the exchangeable bases and carbonates. They were then shaken with increasing amounts of alkalis, and the relation between pH and  $E_h$  was determined. This relationship was found to be linear for all soils, irrespective of the nature



of the alkali used for titration. Some typical curves showing this relation are given in figure 1. The slopes of such straight lines for a number of soils are given in table 2. They indicate millivolts of change in potential for every unit change in pH. These values were obtained by the method of least squares, though a less accurate value could be obtained graphically by fitting a straight

TABLE 2  
*Change in potential in millivolts (Slope) for unit change in pH*

SOIL NUMBER	SLOPE	SOIL NUMBER	SLOPE	SOIL NUMBER	SLOPE
<i>M Series</i>		<i>P.C. Series</i>			
1	59.5	2	68.5	48	39.3
2	58.7	4	37.4	49	46.5
3	66.1	6	69.7	50	67.5
4	44.4	7	56.44	53	65.3
5	43.0	9	54.8	54	56.5
6	63.1	10	48.9	56	31.18
7	56.8	11	41.8	57	60.96
8	51.8	12	68.5	58	35.72
9	67.5	14	51.03		
10	60.3	17	55.1		
11	53.8	20	53.5		
12	46.2	21	47.8		
13	52.2	26	73.1		
14	40.6	27	26.8		
15	46.0	28	28.8		
16	57.2	29	39.09		
17	63.0	30	65.0		
18	64.5	31	55.4		
19	56.5	33	76.3		
20	56.5	39	64.5		
21	54.0	44	57.52		
22	64.9	45	68.73		
23	50.1	47	27.69		
<hr/>					
Gelatin .....		65.61			
Humic acid .....		52.36			
Iron silicate.....		65.02			
Aluminum silicate .....		32.63			

line to the pH —  $E_h$  values. It will be seen that the mean value of the slope for all the soils is of the order of 53.4 millivolts.

It is remarkable that Michaelis (3), some years ago, pointed out the analogy between the micellas of a colloid acid (acidoid) and a metallic platinum-hydrogen-electrode, and ventured the conjecture that the potential of such an electrode might depend on the hydrogen-ion concentration according to the same logarithmic rule as the potential of a metallic electrode, that is, a varia-

tion of one pH unit should correspond to a change of 58 millivolts. Michaelis was unable to substantiate this conjecture experimentally while working with mastic particles, and he admitted that the analogy did not hold. We find that his original assumption was fundamentally correct and that his choice of mastic as a typical acidoid was unfortunate. We find that not only is the relation substantially correct for soils, but that other substances, like gelatin, humic acid, and aluminum and iron silicates, all of which furnish ionic micellas and behave as acidoids, give a straight line relation between pH and  $E_h$ , as

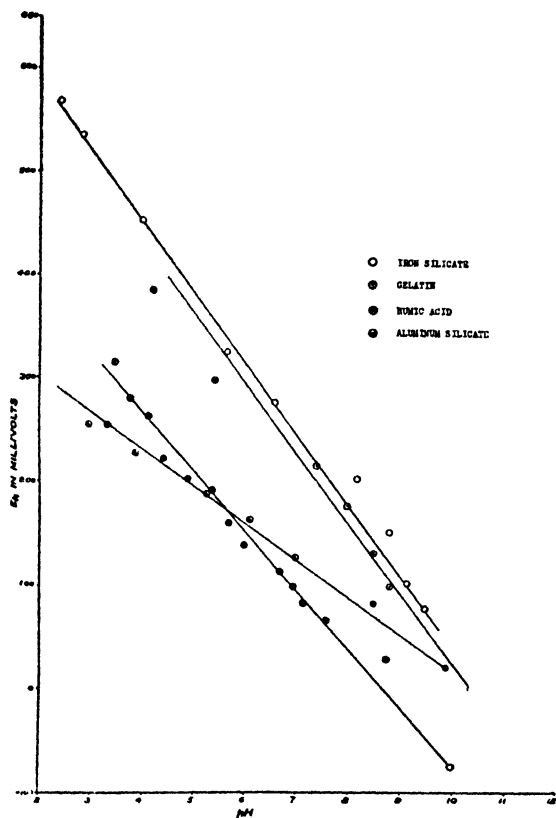


FIG. 2. RELATION BETWEEN pH AND  $E_h$  OF VARIOUS COLLOIDAL SUBSTANCES

shown in figure 2. In a metallic-hydrogen electrode, according to Nernst, the electrode has a tendency to emit hydrogen ions into the solution. On the other hand, the hydrogen ions of the aqueous solution have a tendency to settle on the metallic surface. One or the other tendency prevails, according to the concentration of hydrogen ions in the solution. Exactly the same thing happens in completely unsaturated soil, in which the tendency for the hydrogen ions to be liberated and to diffuse into the aqueous solution is the greater. This tendency is gradually diminished as the acidoid is neutralized with a base.

It will be seen that the thermodynamic relation does not include any factor relating to the quantity of the acidoid, and therefore the  $\text{pH} - E_h$  relation should be independent of the concentration of the soil suspension. A novel application of this principle is that a small quantity of an acidoid could be used for stabilizing the  $\text{pH} - E_h$  relation of an ordinary buffer. This will be clear from figure 3, which gives the  $\text{pH} - E_h$  relation in a series of buffer solutions before and after the addition of small amounts of clay suspension and finely powdered zeolite (sodium-aluminum silicate). The quantities of clay and zeolite added were so small that the  $\text{pH}$  value of the buffer was not affected, yet the potential was stabilised. It will be recalled that only a small quantity of quinhydrone is required to stabilize the  $\text{pH} - E_h$  relation in a

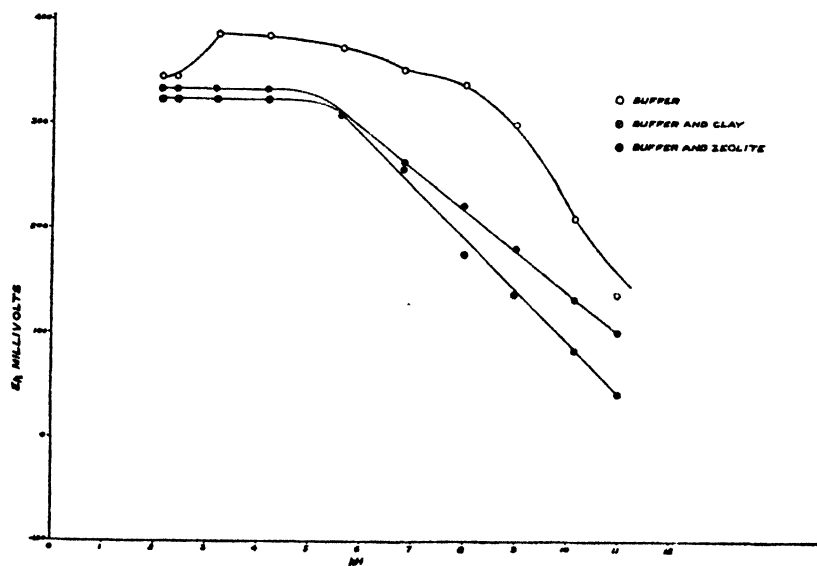


FIG. 3. STABILIZATION OF  $\text{pH} - E_h$  RELATIONSHIP BY CLAY AND ARTIFICIAL ZEOLITE IN BUFFER SOLUTION

solution, and this principle forms the basis of  $\text{pH}$  determinations by the quinhydrone electrode. Similarly, a small quantity of a colloidal solution that behaves as an acidoid could be used for measuring the  $\text{pH}$  value of solutions. The possibility of developing such an acidoid electrode for  $\text{pH}$  measurements should be explored by other investigators. Such an electrode would cover the alkaline range up to  $\text{pH}$  10 and would thus be superior to the quinhydrone electrode.

With such perfect relationship between  $\text{pH}$  and  $E_h$ , it is hardly to be expected that the measurement of oxidation-reduction potentials in soils could lead to results of any greater value than those that could be obtained by  $\text{pH}$  measurements.

## SUMMARY

The so-called oxidation-reduction potential in soils is shown to be a fundamental property of all colloidal substances which furnish ionic micellas and behave as acidoids. The relation between pH and  $E_h$  in soils is so perfect that the measurement of pH should suffice for all practical purposes.

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# A MECHANICAL DEVICE FOR DETERMINING THE PERMANENT WILTING POINT OF SOILS BY MEANS OF THE COHESION METHOD<sup>1</sup>

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The cohesion method<sup>2</sup> has been offered as a rapid and practical means of determining the permanent wilting point of soils. The principle of the method is that at or above the wilting point the soil moisture film is sufficiently thick to cause the soil particles and granules to cohere when lightly pressed together, but below the wilting point the moisture film becomes too thin and discontinuous and is held with such great attractive forces that no such cohesion occurs.

The original procedure of the method consists of placing a small amount of moist soil on a base and lightly pressing the soil with a spatula, which is then quickly lifted. If the soil moisture is at or above the wilting point, the soil particles will stick to one another and to the spatula and will be lifted as a pressed soil mass or bar; and if the moisture is below the wilting point, the soil particles will not cohere, nor will they adhere to the spatula.

The accuracy of the method depends to a considerable degree on the amount of pressure that is applied to the soil by the spatula. Since the pressure applied to the spatula is by the hand, it is evident that the personal element enters into the technic and the experimental results are bound to vary with different operators. An automatic device for pressing the soil uniformly and thus eliminating the personal element in the technic thus becomes essential.

It is the purpose of this paper to present such a mechanical device, which increases the convenience, accuracy, and reliability of the cohesion method for determining the wilting point of soils. This mechanical device can also be used under field conditions to ascertain whether the field moisture is at, above, or below the wilting point.

## DESCRIPTION OF MECHANICAL DEVICE

The mechanical device developed is shown in plate 1.<sup>3</sup> It consists of two rollers, both of which have handles. One roller, made of aluminum, is 2

<sup>1</sup> Authorized for publication as journal article 324, n.s., of the Michigan Agricultural Experiment Station.

<sup>2</sup> Bouyoucos, G. J. 1938 A rapid method for determining the permanent wilting point and for indicating under field conditions the relation of soil moisture thereto. *Soil Sci.* 45: 47-55.

<sup>3</sup> The base and roller shown in plate 1 are manufactured by the Metal and Wood Products Co., Bloomfield Hills, Michigan.

inches long, 1 inch in diameter, and weighs about 73 gm. This roller is to be used for all soils except the heavy, sticky clays. The other roller, made of brass, is 1-5/8 inches long, 1-5/8 inches in diameter, and weighs about 500 gm. This second roller is to be used only for the heavy, sticky clays. These rollers are allowed to rest on the base, and by means of the handle, they are slowly and gently rolled over the soil. Since their weight is constant and rests on the base, the pressure they exert on the soil when they are rolled over it tends to be uniform.

The following pieces of apparatus are required for the operation of the method with the special rollers:

Two special rollers.

A base painted with asphalt paint, waxed, and polished so that the soil will not stick to it.  
A medium-sized 2-mm.-mesh sieve.

A small bottle of pure methyl alcohol. The neck of the bottle should be wide enough to permit the rollers to be dipped into the alcohol.

A pint Mason jar with cover.

An oilcloth about 12 inches square

A medium-sized soil pan.

A 10-cc. pipette.

A small 3-inch-blade spatula.

For determining whether the soil moisture under field conditions is at, above, or below the wilting point, the procedure consists of taking a sample of the soil to be examined, screening it rapidly on the oilcloth, and putting it into the Mason jar. By means of the spatula, about 3 gm. of the soil is placed on the base and spread thickly (1/16 inch) and evenly without being compacted. The spreading or leveling is done by the edge of the spatula. The roller suitable to the soil type is dipped into the alcohol, shaken vigorously several times to throw off any excess alcohol, brought to rest on the base near the soil, and then, by means of the handle, it is slowly and gently rolled over the soil and lifted. If the soil moisture is at or above the wilting point, the soil particles will stick to one another and to the roller and will be lifted as a pressed or rolled soil mass (pl. 1); and if the soil moisture is below the wilting point, the soil particles will not cohere, nor will they adhere to the roller.

For determining the wilting point of soils in the laboratory by this improved cohesion method, the procedure is as follows: Approximately 50 gm. of an air-dry soil is weighed out and placed in a medium-sized soil pan. A definite amount of water is added to the soil, which is then mixed by hand, screened, mixed again, put into the Mason jar, and covered to prevent loss of moisture. The soil is then subjected to the sticking tests already described. If the test is negative, that is, if the soil particles do not stick to one another and to the roller, more water is added and mixed with the soil. The procedure of adding more water and mixing the soil thoroughly is continued until a positive test is obtained. At this point the total moisture is determined in the usual manner, and this moisture content represents the wilting point of the soil.

The number of additions of water to the soil and the quantity of water to be added at the outset depend on the type of soil. If the soil, for instance, is sand, the wilting point of which may be about 2 per cent, only about 0.5 cc. of water is added at first to 50 gm. of soil. If the soil is a clay loam, which has a wilting point of about 20 per cent, 7 or 8 cc. of water is added at first, and 0.5 to 1 cc. after each test. In this manner the procedure can be carried out fairly rapidly.

#### COMMENTS

The improved cohesion method, using the automatic device instead of the spatula, has been compared with the direct method and the dilatometer method of determining the permanent wilting point of soils. The results obtained are essentially the same as those presented in the first report, namely, that the cohesion method tends to give virtually the same wilting point determinations as do the other two methods. This is generally true in all the types of soil except in the extremely sticky clays as typified by Houston clay, McKenzie clay, and some of the clays of the lower soil horizons. In such extremely sticky clays the method is not highly accurate because of the great difficulty of sieving these clays and thereby bringing about a thorough and even distribution of the moisture on all their particles. For such extremely sticky clays, the dilatometer is the most accurate method of determining the wilting point. On the other hand, the method works fairly satisfactorily on clays which contain a considerable amount of silt or organic matter and which are not extremely sticky, such as Yolo clay, Capay adobe, and Davidson clay. With patience and care, the method can be made to work satisfactorily even with the extremely sticky clays.

Soils that have an appreciable content of salts tend to give a lower wilting point with the cohesion method than they do with either the direct method or the dilatometer method. This is probably because the cohesion method measures the wilting point that is due mainly to the physical attractive forces of the soil for the water, whereas the other two methods measure, in addition, the wilting point that is due to the salts. The differences, however, are small unless the soil contains large amounts of soluble salts.

When the wilting point is being approached the soil begins to stick and to lift partially and irregularly. This is not the point at which to stop. Additional amounts of water should be added until the soil sticks and lifts in a clear-cut manner without any dust being left behind (pl. 1) and until the same result can be obtained repeatedly. When the soil reaches the true wilting point it ceases to be in a powder form, and its original color changes because of the thicker moisture film that is formed around the soil particles. After the soil reaches the wilting point, additional water does not increase perceptibly its sticking and lifting phenomena as measured by this method. Very little water need be added, therefore, after the soil shows signs of sticking and lifting.



Silts tend to allow a premature cohesion and lifting to take place. When this occurs, it is noted that the base is not clean but is smeared with dust. The true wilting point is reached when the lifting of the soil leaves no dust behind and the base is absolutely clean. This is a very important point to watch, especially with silts.

All soils should be passed through a 2-mm.-mesh sieve and thoroughly mixed so that the moisture will be well distributed throughout the mass, which must be in a loose and granular condition. When the method is used in the field the sieving and mixing procedure should be done as rapidly as possible in order to avoid evaporation.

After the 50 gm. of soil is mixed with a definite amount of water and put into the Mason jar, any portion of the soil that is taken out for testing is returned to the jar when the test is completed. This is done by scraping the soil off the roller and off the base into the Mason jar. In this way one knows how much water to add for an approximate increase in water content. When the wilting point is approached the soil should be left in the jar for a few minutes after an addition of water, to allow the water to wet and to penetrate the soil particles thoroughly.

The object of dipping the roller in alcohol is to form a thin film on the roller and thus to facilitate the adhesion and lifting of the soil mass. This alcohol film is analogous to the water film around the soil particle. Any liquid can be used, but alcohol is very convenient for forming a thin film. When taken out of the alcohol, the roller should be shaken vigorously several times in order to throw off any excess alcohol and leave only a very thin film.

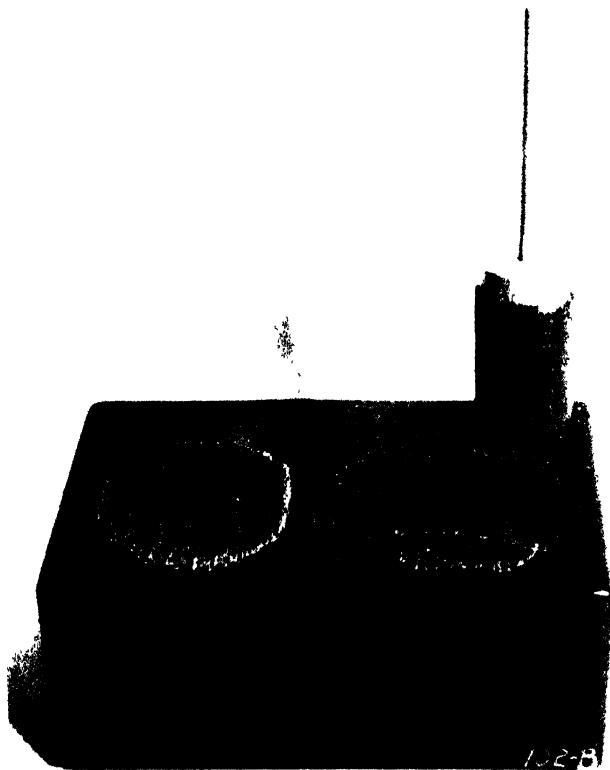
When the soil, especially clay, is being wetted by the addition of water, it indicates a slightly lower wilting point than it does when it is being dried by evaporation. This is due partly to hysteresis and partly to the difference in the moisture content between the outer and the inner surface of the soil granules in the two procedures.

An attempt should be made always to take about the same volume of soil and to spread it evenly about 1/16 inch thick.

The 500-gm. roller should be used only for the heavy, sticky clays and not for the light soils. Because of their granular condition after being sieved, the true clays need to be pressed considerably harder than do the light soils.

#### PLATE 1

BASE, ROLLER, PILE OF SOIL BEFORE BEING PRESSED AND AFTER BEING PRESSED, AND  
PRESSED SOIL LIFTED BY ROLLER





# ON THE FORMATION OF STRUCTURE IN SOIL: VI. METHOD OF MICROSCOPIC INVESTIGATION OF SOIL STRUCTURE IN REFLECTED LIGHT

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The chief thesis of the theory of structure formation, developed by the author, is that the components of soil—sand, clay, humus, oxides—form particular combinations, which are mechanical mixtures, subject to definite laws.

The distribution of these components and their mutual orientation were studied in mixed formations isolated from soil (9) and in models representing mixtures of soil components (10). It proved possible to study, by optical, X-ray, and physicochemical methods, the properties of these mixed formations, both isolated from soil and prepared artificially. Studies by all these methods consistently showed that the union of the individual components of soil is due primarily to molecular forces, that is, to cohesion which is similar to attraction. Interaction between individual particles depends on their reciprocal orientation. Evidently, the particles can have no more favorable orientation than a parallel disposition along the line uniting two particles. The energy of interaction in this case is attractive force, the so-called "orientation effect" by which Keesom (2) explains the attraction of Van der Waals.

For the solution of problems bearing on the formation of soil structures, the introduction of the conception of definitely associated groups may prove more useful than the conception of the rôle of the absorbing complex and the absorbed bases in the soil. The existence, in soils, of structures similar to those described by the author for various mixtures of the individual components of soil (9, 10), may be presumed. It appeared, therefore, that further progress of the author's theory of structure formation might consist in the development of a method of investigation by which evidence of this might be obtained. After some preliminary work, it was found possible to use for this purpose a method of studying structure in polished sections prepared by methods similar to those used in mineragraphy (5, 6, 7, 14, 16) and metallography.

## THE METHOD OF PREPARING POLISHED SECTIONS

Compact hard soil samples, free from large grains of sand or of other mineral elements, can be readily polished without the use of any cementing substance. The sample is polished first on a lathe of the type which is used for polishing minerals and which is fitted with a horizontal iron disk rotated by an electric

motor, fine corundum powder (the so-called "one minute" No. 15) moistened with water being used as the abrasive. Polishing on the lathe is continued just long enough to produce a flat surface. The next operation consists in polishing by hand on a glass plate, finer powders ("one minute" Nos. 120 and 240) being used this time. The sample is then polished on a small lathe, the disk of which is covered with chamois. With these methods, polished samples of different clay rocks, such as the Crimean "kil," Zhuravlin galloisite, and "volkonskonite" (clay containing chromium oxides), as well as samples of dried sols and gels of soil colloids and clay suspensions, were easily prepared. All these reflected light from their surfaces so well that they were readily photographed with the aid of the opaque-illuminator described by Van der Veen (14).

The polishing of clay rocks or soils containing sand or other mineral fragments presents much greater difficulties than does that of solid clay. The chief difficulty is in the heterogeneity of the material. In comparison with the clay minerals, the grains of quartz or of other minerals are much harder and more resistant to treatment. As a result, hollows and uneven places, hindering the further polishing of the sample, are formed. Colophony or fir resin was used, therefore, as cementing material for such samples. The material was dissolved in xylene (1:1), and the samples were immersed in this solution, which was slightly heated to facilitate permeation. As is known from earlier works (8) and from my recent observations, permeation of soil with an "inert" liquid does not disturb or distort the soil structure. It must be noted that when a soil sample is immersed in a viscous solution of colophony or fir resin the penetration of the cementing substance is limited to the surface layer of the sample. Polishing, therefore, must be done very cautiously, otherwise the cemented layer may be worn off entirely by prolonged polishing on the lathe and the cementing will have to be repeated. A suitable method of polishing is that elaborated for friable rocks of sedimentary origin (3, 4).

With some experience, the polishing of cemented samples, even those of small size, becomes easy. For samples of the shape of small grains, the method usually applied to small grains of minerals is recommended. The grains are cemented, melted into a plastic mass, and then polished in the manner already described. The method of polishing cemented samples by hand is similar to that of polishing uncemented samples, and the burnishing is done, likewise, with chamois. With most samples, we were able to obtain polished sections with good reflecting surfaces, a necessary condition for the microscopic study of structure.

#### LAMINAR STRUCTURE OF CLAYS

In earlier works of the author (9), it was established that in drying clay gels, a laminar structure becomes clearly visible, by reason of a great number of dark lines lying parallel to the length of the structural formation. These

lines, which are visible in natural light as well as between the Nicol prisms, show that the particles of clay are arranged in equidistant layers.

In studying polished sections of various clays in reflected light, a laminar structure having the same characteristic features as those of colloidal clay is observed. Figure 1, plate 5, a polished clay section ("volkonskonite"), illustrates this resemblance; it clearly shows how the particles of clay unite into equidistant layers. A similar laminar structure was manifested not only by samples of the Crimean clay "kil" and of the Zhuravlin galloisite, but also by polished sections prepared from dried gels of clay suspensions.

Figure 2, plate 5, shows the structure of a gel lamina obtained, by slow drying, from a Na-sol isolated from a covered clay (clay "Toida"). The clay sol was evaporated in a Petri dish. The lamina of desiccated gel was not polished. Its structure shows some features resembling those of the structure of a clay rock taken during the construction of the Moscow underground railway (the so-called "red clay," belonging to the Carbon period). This clay contains much fine quartz sand, which cannot be separated from clay colloids. The structure of this clay is shown in plate 5, figure 3, which clearly indicates *that there is no sharp limit between the grains of sand and the clay substance* (pl. 5, fig. 2). This indicates that sand-clay mixtures are subjected to the law of *mutual orientation with formation of a laminar system* possessing anisotropic properties (10).

#### STRUCTURE OF SOIL

Because of its practical importance, the structure of the superficial horizons of soil enriched with humus is of particular interest. Earlier researches of the author concerning the interaction of the organic matter and the mineral fractions of soil have shown (10) that the organic matter may be considered as a "metasomatic" substance, which transforms the parent rock and endues it with new properties.

The characteristic feature of this interaction is that no chemical reactions, probably, take place. The component parts of the mixed organic matter-clay formation occupy several states of relative equilibria (10). One of these corresponds to the growth of the clay crystal at the expense of "foreign" material, that is, organic matter, and represents a kind of pseudomorphosis. Another state of equilibrium corresponds to the isotropic condition of humus, which is characterized by a lesser stability of the bond between humus and clay. In each of these cases, we are dealing with a nonhomogeneous formation, consisting of two homogeneous substances, the particles of which are mutually oriented in different ways.

The maximum strength of the bond between the organic matter of soil and clay should be observed at the point at which the anisotropic particles of clay act on the isotropic humus in such a way that the particles of humus become anisotropic. In this case the mixed clay-humus formation must have a structure similar to that of pure clay (10).

The method of polished sections supplies fresh corroboration of this viewpoint. The following experiment was arranged. Flat laminas of desiccated Na-sol isolated from clay "Toida" were cemented with the following sorts of humates: a humate isolated from peat (Na-humate, which I have used in all my experiments); a water extract of decomposed manure, freed, by dialysis, of the admixture of salts and then concentrated by evaporation at a low temperature; and a humate obtained from brown coal (supplied by Z. J. Lein). The cementing, in every case, was done with a drop of humate placed between the laminas of clay. The set was almost instantaneous. After the desiccation of the laminas of clay, a cross section, including the laminas and the cementing substance between them, was polished. Microscopic examination of this section showed that the cementing layer of humate in close contact with the laminas of clay acquires a laminar structure indistinguishable in its characteristics from the laminar structure of clay. The rest of the humus does not form a laminar structure. The different kinds of humates employed for cementing the laminas of clay behaved similarly, as was shown by microscopic examinations of cross sections, and their structure was not different from that shown in figure 4, plate 5. Thus, this photograph may serve as an illustration of the orientation of humus particles in relation to clay and as a confirmation of the theory that clay is the substance which directs crystallization of humus.

On the basis of these observations, the conclusion may be drawn, that the formation of a watertight structure in soil is determined by the orientation most favorable to the forces of attraction, that is, parallel disposition of the particles of the mixed clay-humus formation. The checking of this conclusion on durable structure is of considerable interest and is achievable only by the technic employed for these structure studies.

Different samples of structural soils, the stability of which was checked by means of aggregate analysis, that is, by resistance to the destructive action of water, were chosen for observation. Among these were several samples of the solid granular structure of chernozems, of the solid structure of weak solonetz soils (supplied by V. V. Bernikov), and of watertight aggregates of a podzol soil from under clover (supplied by F. J. Heltzer from an experimental field of the Timiriazev Agricultural Academy).

The polished sections prepared from these water-resistant structural forms showed under the microscope *all the peculiarities of structure which characterize the presence of a firm bond* between the individual components of soil. This is illustrated in plate 5, which shows a polished section of the granular structure of a weakly leached chernozem from the Irtysh steppe (fig. 5), a columnar solonetz from West Siberia (fig. 6), and a watertight aggregate of podzol soil from under clover (fig. 7). In every one of these structures the particles of the mixed clay-humus formation are arranged in parallel layers.

The orientation of the particles of a mixed formation is so characteristic a feature for judging the firmness of the bond that it can be utilized for various

purposes, for example, for the comparative study of the structures of different horizons of a soil.

Utilizing the analysis of the structure of the plowed and underlying layers of a soil from the Kuznetzk Experiment Station, made by Vladychensky (14) according to the method of Tyulin (13), I made a comparative study of the structure of these horizons. Figure 8, plate 5, shows a polished section of soil from the plowed layer; figure 9, a polished section from the underlying layer. It is apparent from these photographs that we are dealing with soil formations related by their genesis but differing in that the bond between the particles of soil from the plowed layer is considerably weakened in comparison with the underlying layer. This observation corresponds with the results of the analysis made by Vladychensky (14).

It is necessary to dwell on one more observation of some significance in the clarifying of our theories regarding the influence of absorbed sodium on structure. It is well known that chernozem soil, saturated with sodium, becomes very unstable in regard to water, though it acquires considerable mechanical resistance. It is also known that chernozem soil, saturated with sodium under pressure, becomes watertight. My observations on Kamennaya steppe chernozem, saturated with sodium and then slightly washed with water to eliminate the salt, showed that the soil retains its macrostructure, provided it is left standing undisturbed, not only in water but also in an alkaline solution; even after the elimination of a considerable part of the organic and mineral colloids, the macroaggregates showed considerable stability and did not disintegrate when stirred with a glass rod (12).

Microscopic study of its structure explains the behavior of this soil; the structure is represented in plate 5, figure 10. Patches of disoriented black particles are visible amid particles oriented into parallel rows. As is shown by analysis, these disoriented areas do not consist of humus alone, but include mineral colloids as well (12). The presence of nonoriented particles is the cause of the loss by the soil, when elutriated gently in water or in a solution of NaOH, of those particles which are not associated into groups, that is, the disoriented part. On the other hand, those particles of the mixed formation which are oriented in rows remain, thus determining the shape and stability of the macroaggregates, in spite of the fact that these macroaggregates have remained for a long time in water or in a solution of alkali (12). The laminar structure of these aggregates is confirmed also by observations on thin polished sections of the same Kamennaya steppe soil between Nicol prisms (pl. 5, fig. 11). As is to be expected, the laminar formation, consisting of the sand-clay-humus mixture, is doubly refracting. There is no sharp limit between the individual components of the mixture. Sand, clay, and humus appear as a homogeneous mass with a uniform structure. Only a few coarse grains of sand escape from the general grouping.

When the amount of humus in the clay-humus mixture exceeds the number



of centers of crystallization, excess humus assumes the state of equilibrium corresponding to its isotropic condition. When such a mixture is desiccated it separates into two different parts: one, the anisotropic, has a high viscosity and is a pseudomorphous formation of humus on clay; the other, the isotropic, is less viscous and consists of humus. The disintegration of such a mixture is due to the surface tension of isotropic humus, which is nearly equal to that of water and which causes the humus to accumulate on the periphery of the more viscous anisotropic formation (11). The photographs of a humus-rich columnar solonetz from Volchia River (pl. 5, fig. 12 and 13) may serve as evidence that this phenomenon is encountered in soil. They represent polished vertical (fig. 12) and horizontal (fig. 13) sections of a columnar solonetz aggregate. It is evident that the structures of the sections are alike. Their characteristic feature is the structure of microaggregates about 0.3–0.5 mm. in size. The structure of these microaggregates corresponds exactly to that of a disintegrated clay-humus mixture containing excess organic matter (10, 11). The "amorphous" envelopes of isotropic humus deposited on the periphery of the anisotropic formation, which occupies the central position, are clearly visible in figures 12 and 13, plate 5. The anisotropic properties of this formation can be clearly distinguished in plate 5, figure 14, taken from a thin polished section of solonetz between crossed Nicol prisms.

#### STUDY OF STRUCTURAL CHANGES

As an example of a structureless soil, we may take a serozem from the Ak-Kawak Experiment Station (Central Asia). According to Heltzer (1), the watertight microaggregates (0.25–1 mm.) in this soil constitute only about 1.5 per cent of the total. Examination of polished sections prepared from the soil showed an almost complete absence of oriented groups of particles (pl. 6, fig. 1).

As the experiments of Heltzer have shown, the introduction of an insignificant amount of the autolytic products of the fungus *Aspergillus niger* completely transforms the structureless soil into a structural soil containing 99.6 per cent of stable macroaggregates (1). These structural changes were followed in several samples of the Ak-Kawak serozem moistened with the products of autolysis of *Aspergillus niger*. Several polished sections were prepared, all of which showed the same picture of alterations (pl. 6, fig. 2). Envelopes of another substance with a pronounced tendency to an oriented arrangement of particles, forming at the surfaces of delimitation of the separate disoriented groups of particles, are clearly visible in this figure. It is evident that the appearance of oriented envelopes is the cause of the abrupt rise in the stability of the serozem structure. It is noteworthy that this observation on the oriented arrangement of particles is in accordance with the previously established ability of autolytic products to form laminar systems manifesting strong double refraction.

Besides serozem, samples of chernozem from the Plavsky Machine and

Tractor Station were also investigated. This soil, according to Heltzer, has a very unstable structure. The samples, moistened with autolytic products of *Aspergillus niger* so as to produce thick and thin envelopes of this substance, were studied with regard to the structural changes taking place. Polished sections were prepared from every sample. Figure 3, plate 6, shows a sample of this soil untreated by the products of autolysis. The presence of disoriented groups of particles indicates that the soil is almost structureless. Quite a different picture is revealed by the photographs made from the samples of Plavsky chernozem covered with a thin layer (pl. 6, fig. 4) or a thick layer (pl. 6, fig. 5) of autolytic products. These figures show that the introduction of a small amount of the substance (fig. 4) changes completely the grouping of particles, endueing it with features characteristic of a stable granular structure (compare plate 5, figure 5). This confirms again the general rule concerning the high cementing capacity of thin layers of adhesive substances. The adhesive material is here limited to a very small volume in direct contact with large particles. The structure of the thick envelopes of autolytic products is clearly visible in figure 5, plate 6. The central part of the figure, representing the area of weakly oriented or quite unoriented groups, is surrounded by a thick layer of autolytic products having a characteristic structure.

An illustration of the influence of fertilizers and of agrotechnical methods on the structural changes in soil, is presented in field experiments with sugar beets in a two-field crop rotation of peas and sugar beets, arranged at the Suma Agricultural Experiment Station. The scheme of the experiments from which the soil was taken was as follows: Experiment 1. Control, no fertilizers. Experiment 3. Every second year, 60 kgm.  $P_2O_5$  as superphosphate + 90 kgm.  $K_2O$  ( $K_2SO_4$ ). Experiment 4. Every second year, 52 tons of manure. Experiment 18/20. Under sugar beets in the pea-sugar beet crop rotation, 52 tons of manure (12). The structure of soil samples from these experiments was studied in detail by means of aggregate analysis and by a special method of colloid-chemical separation (12).

The results of these analyses are in accordance with those of the microscopic studies of structure in polished sections. Figures 6-9, plate 6, represent samples of soil taken from experiments 1, 3, 4, and 18/20. Figure 6 (control experiment) shows fewer oriented particles than do the others. The characteristic feature of the soil structure of the control experiment is that the individual quartz grains are scattered irregularly, thus showing the lack of structure. The structure of soil from experiment 4 (fig. 7) bears a general resemblance to that of the control experiment, but differs from the latter in having a higher content of oriented particles in laminar formations, easily discernible in different parts of the photograph. The composition of aggregates and the results of the colloid-chemical analysis show that the soils of experiments 1 and 4 are, indeed, very similar, differing to only a slight extent in their macroaggregate (0.5 mm.) content and in the loosely held fraction of the colloids (12). The structure of soil from experiment 3, with mineral ferti-

lizers (fig. 8), contains more oriented particle groups than that of soil from experiment 4, but quartz grains are still easily discernible here. This structure change corresponds to the analytical results: the quantity of macroaggregates (0.25–0.5 mm.) increases to 17.5 per cent as compared with 9.05 per cent in the control. The structure of soil from experiment 18/20, treated with manure in a pea-sugar beet crop rotation (fig. 9), differs from the others in that here the quartz grains are almost indistinguishable and represent an integral part of the laminar formations that are typical of the entire polished section. There is here no loosely held colloidal fraction (disoriented particles). The quantity of aggregates (0.25–0.5 mm.) is almost equal to that of the soil from experiment 3.

On the basis of this study of the structure of the soils of experimental plots treated with manure, it is impossible to draw the conclusion that a supply of "amorphous," that is, loosely bound, humus has formed in the soils under the influence of manure. The soil is "unsaturated" with humus, as is evidenced by the results of the colloid-chemical analysis (12).

#### SUMMARY

The observations described furnish grounds for the belief that the method of studying structure in reflected light by means of polished sections can be applied to the solution of a number of practical questions bearing on agrotechnical methods and the use of fertilizers. The method proved very sensitive in observations on structure changes and can, therefore, be used as a control and for purposes of comparison with other methods of soil structure analysis. The significance of this method is not limited to its applicability to practical problems. Microscopic study of structure may be utilized for the explanation of questions bearing on the genesis of soils, and particularly those on soil morphology. In problems of morphogenesis and in establishing the relation between the form of structural varieties and the inherent properties of soil, this method may be of considerable service, and may be of help in obtaining knowledge of the properties of soil.

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## PLATE 5

FIG. 1. The polished clay section "volkonskonite." Magnification  $\times 20$ .

FIG. 2. The structure of lamina of desiccated gel (Na-clay "Toida"). Magnification  $\times 20$ .

FIG. 3. The polished section of "red clay." Magnification  $\times 20$ .

FIG. 4. Cross section of the clay lamina ("Toida") and the adhesive material (Na-peat humate). Magnification  $\times 23$ .

FIG. 5. Watertight aggregate of the granular structure of weakly leached chernozem. Magnification  $\times 23$ .

FIG. 6. Watertight columnar alkali soil. Magnification  $\times 23$ .

FIG. 7. Watertight aggregate of a podzol soil. Magnification  $\times 23$ .

FIG. 8. The plowed layer of the soil from the Kuznetzk Experiment Station. Magnification  $\times 23$ .

FIG. 9. The underlying layer of the soil shown in figure 8. Magnification  $\times 23$ .

FIG. 10. The chernozem soil (Kamennaya steppe) saturated with sodium and slightly washed with water. Magnification  $\times 23$ .

FIG. 11. The soil shown in figure 10, between Nicol prisms. Magnification  $\times 23$ .

FIG. 12. The columnar alkali soil from Volchia River. The vertical section. Magnification  $\times 23$ .

FIG. 13. The soil shown in figure 12. The horizontal section. Magnification  $\times 23$ .

FIG. 14. The soil shown in figure 12, between Nicol prisms. Magnification  $\times 23$ .

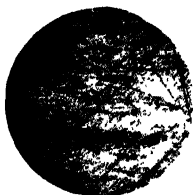


FIG. 1

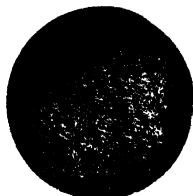


FIG. 2

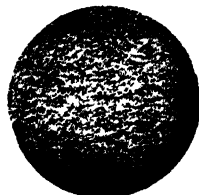


FIG. 3



FIG. 4



FIG. 5

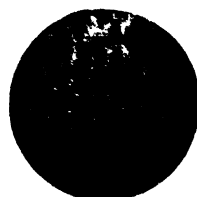


FIG. 6



FIG. 7

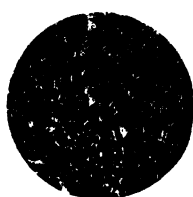


FIG. 8

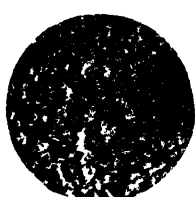


FIG. 9



FIG. 10



FIG. 11



FIG. 12



FIG. 13

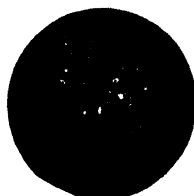


FIG. 14

## PLATE 6

FIG. 1. The serozem soil from the Ak-Kawak Experiment Station. Magnification  $\times 23$ .

FIG. 2. The soil shown in figure 1, treated with the products of autolysis of *Aspergillus niger*. Magnification  $\times 23$ .

FIG. 3. The Plavsky chernozem soil. Magnification  $\times 23$ .

FIG. 4. The Plavsky chernozem covered with a thin layer of autolytic products of *Aspergillus niger*. Magnification  $\times 23$ .

FIG. 5. The Plavsky chernozem covered with a thick layer of autolytic products of *Aspergillus niger*. Magnification  $\times 23$ .

FIG. 6. The chernozem soil of Suma Agricultural Experiment Station. Control experiment. Magnification  $\times 20$ .

FIG. 7. The soil shown in figure 6. With 52 tons of manure. Magnification  $\times 20$ .

FIG. 8. The soil shown in figure 6. With mineral fertilizers. Magnification  $\times 20$ .

FIG. 9. The soil shown in figure 6. With 52 tons of manure in a pea-sugar beet crop rotation. Magnification  $\times 20$ .



FIG. 1



FIG. 2

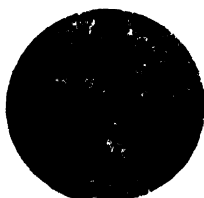


FIG. 3



FIG. 4



FIG. 5

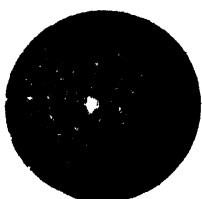


FIG. 6

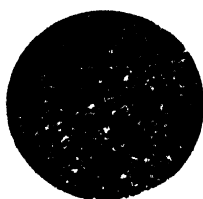


FIG. 7

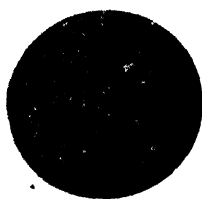


FIG. 8

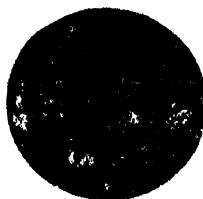


FIG. 9





# THE INFLUENCE OF ENVIRONMENTAL FACTORS ON NUMBERS OF SOIL MICROORGANISMS

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In a previous paper the author (11) gave a preliminary account of the general chemical and microbiological features of an English pasture soil under conditions of treatment which involved various combinations of manuring and irrigation. As a result of this work it was concluded that in grassland soils the upgrade and downgrade processes of the nitrogen cycle were no different in nature from those in arable soils, and that the observed differences in the levels of intensity of these factors were purely those which would be expected in view of the nature of the crop occupying the soil. It was concluded also that moisture exerted a controlling influence on numbers of bacteria, actinomyces, and fungi, in that numbers of these groups of organisms as indicated by plate counts were increased as a result of irrigation. At the same time, it was also suggested that the reduced numbers of these organisms which were recorded during the late autumn and early spring resulted from the lower soil temperatures then prevailing. The data, which consisted of weekly observations throughout the greater part of the year, have now been subjected to statistical treatment in an attempt to isolate the effects and to assess the relative importance of such environmental factors as soil moisture content, soil temperature, and soil reaction.

## STATISTICAL TREATMENT OF THE DATA

The regressions of numbers of bacteria (*b*) and actinomyces (*a*) in millions/gm. dry soil, and fungi (*f*) in thousands/gm. dry soil, on moisture (*m*) as percentage of dry soil, temperature (*t*) in Fahrenheit degrees at 4-inch soil depth, and pH, during the 24 weeks period for which data were available, were investigated.

At the outset, some explanation is necessary concerning the particular method of analysis used. The figures, which exist for four differently treated plots (the four combinations of nitrogen, no nitrogen, irrigation, no irrigation), were formally analyzed as though they constituted a straightforward multiple

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regression problem. The inadequacy of this analysis, by itself, is considered in the discussion following the results. A much more complete analysis was in fact possible, for not only could the variation have been split up into positional (that is, treatment) and time effects, but the latter could have been divided further into long-term trends and short-term fluctuations. It should be pointed out, however, that if we are regarding the importance of different sources of variation in the number of organisms as proportional to the magnitude of the changes they produce, a major problem will be an explanation of the seasonal changes observed on the different plots. From this point of view, it is believed that the formal analysis made, provided it is associated with the discussion and the further statistical points made, has extracted practically all the information to be obtained from the data, and is a useful compromise in view of the very much greater computational labor attaching to any more complete analysis, and the limitations that, whatever the statistical treatment, this kind of data must inevitably have, if a consideration of trends is to be included.

TABLE 1  
*Variance extracted for different factors ( $\times 10^4$ )*

	D.F.	<i>b</i>	<i>a</i>	<i>f</i>
<i>m</i> .....	1	26,971.1*	13,988.8*	183.9
<i>t/m</i> .....	1	111.9	14,790.5*	7,781.6*
<i>tm/t, m</i> .....	1	394.9	35.7	468.2
<i>pH/tm, t, m</i> .....	1	9.6	2,621.6†	719.8
Residual.....	91	330.3	452.0	319.5

\* Significant,  $P = 0.01$  (see below, however).

† Significant,  $P = 0.05$  (see below, however).

Since it might be expected that variation in bacterial numbers would be directly proportional to the numbers themselves, the analysis was carried out on the logarithms of the numbers. The fluctuations observed justified this expectation and were made more comparable by this transformation. The fairly close relationship with moisture was also made more nearly linear. For consistency the logarithms of numbers of actinomyces and fungi were also used. In order to make sure that there was no evidence of an interaction between the effects of moisture and temperature on bacterial numbers, the variate *tm* was added.

Table 1 summarizes the results obtained in an analysis of variance form. The fraction of the variation in numbers of organisms that is expressible in terms of the "independent variates" *m*, *t*, *tm*, and *pH* has been extracted in stages corresponding to these variates in the order given. Thus the first row gives the variance corresponding to the simple regression on *m*; the second row, the extra variance accounted for in terms of *t* when this regression on *m* has already been eliminated, and so on. In this form the analysis of variance table is additive, and the total variance accounted for can be seen at a glance.

In table 2 are recorded the partial regression coefficients on  $t$ ,  $m$ , and pH. Since from table 1 it can be seen that the inclusion of the variate  $tm$  has served no useful purpose, this has been omitted in preparing table 2.

The correlations between the "dependent variates" are given in table 3. The partial coefficients are those obtained after the elimination of the "independent variates."

It should be borne in mind that the foregoing regressions and correlations refer to the units in which the analysis was conducted, namely, *logs*.

Before any interpretation of the foregoing results can be attempted, some discussion is essential on the type of data that has been analyzed. In the first place, the dependence of bacterial numbers on external conditions such as moisture and temperature is a problem which theoretically could be most

TABLE 2  
*Partial regression coefficients on  $t$ ,  $m$ , and pH*

	$b$	$a$	$f$
$t/m$ , pH.....	+0.00162	+0.01928*	+0.01390*
$m/t$ , pH.....	+0.03560*	+0.05044*	+0.02118*
pH/ $t$ , $m$ .....	-0.0107	-0.2654†	-0.1730

\* Significant,  $P = 0.01$  (see below, however).

† Significant,  $P = 0.05$  (see below, however).

TABLE 3  
*Correlations between  $b$ ,  $a$ , and  $f$*

	SIMPLE	PARTIAL
$r_{ab}$ .....	+0.4673	+0.2778
$r_{bf}$ .....	-0.0706	-0.2306
$r_{af}$ .....	+0.1559	-0.1551

simply answered by a controlled experiment; but this is hardly possible in practice. (It should, however, be remembered that the irrigation of two of the plots modified the environment to the extent of producing a marked differential maintenance of moisture level during the driest spell.) The substitution of observational material must introduce limitations which will vary with any set of data available. The fluctuations will, for example, be different according as the data are similar observations at different places or successive observations at the same place. The data here correspond to the second class, except that four simultaneous observations for four plots exist for each week. There is no reason to suppose that these four observations, after any real effects of moisture, temperature, etc. have been eliminated, will be independent in a statistical sense, and furthermore there is no reason to suppose that the residual values of the successive observations from any one plot will be independent. Although in the statistical analysis these aspects have been formally ignored,

they have been borne in mind in assessing the validity of the conclusions which have been drawn. Finally, there is the important point already referred to, that since a fairly large fraction of the variation of the "independent variates" is fairly simple long-term change, the correspondence between, say, bacteria and one of these variates, even if statistically significant, from the viewpoint of regression, does not necessarily imply a real relationship. It is for this reason that the results have been stated in terms of regression and not of correlation. The terms given as significant are to be regarded only as meriting further examination, those not significant being assumed to be of no value. The dependent variates  $b$ ,  $a$ , and  $f$ , especially after elimination of effects of environment, can be more legitimately regarded as chance variates, in connection with the correlations between them, but here again observations are not independent, so that, although it was of some interest to calculate correlation coefficients, no tests of significance were made. Any real correlations are somewhat reduced by errors in estimating  $b$ ,  $a$ , and  $f$ .

It should be noted that since Jensen (16) also obtained his data under conditions approximating to the second class, namely, successive observations at the same place, the foregoing considerations are equally applicable, although he takes no account of this in making his deductions. For this reason doubt may attach to some of the correlations which he obtained.

With regard to the apparent association with environment, that of bacteria with moisture is greatest and has most claim to be real. Moreover, from a graph the relationship can be traced to some extent in the short-term fluctuations as well as in the trend, which, though markedly different for the irrigated and unirrigated plots, was closely followed in each case by the bacteria trend. Table 1 shows that nearly half the total variance is accounted for in terms of moisture and indicates also the absence of any other factor having any appreciable effect.

Since there appears to be least doubt about the influence of moisture in the case of bacteria, some idea of the magnitude of the effect of moisture on plate count numbers may be obtained with some justification from the partial regression coefficient given in table 1.

$$\begin{aligned}\text{Since } \log b - \log b_0 &= 0.0356 (m - m_0), \\ b/b_0 &= 10^{0.0356(m-m_0)} \\ &= 1.085 \text{ (if } m - m_0 = 1)\end{aligned}$$

That is to say, an increase of 1 per cent in the moisture content is accompanied by an increase of the order of 10 per cent in the numbers of bacteria. (This estimate is, of course, mainly determined by the seasonal variations in moisture content observed in the data.)

The strong relationship which exists between moisture and temperature naturally implies an apparent association between bacteria and temperature, but, with these data, there is no effect of temperature which is not fully accounted for in terms of moisture. The residuals for  $b$ , after elimination of  $m$ , have been plotted, and indicate further the dependence of the bacteria trend on that of moisture, constituting very fair approximations to random series.

The only exception is the series for the unirrigated N-treated plot; this gives a very slight but significant linear trend downward throughout the period, which may be ascribed perhaps to the nitrogen treatment.

It was expected that a relationship would be found with pH. In an attempt to ascertain whether any short-term relationship existed that had been masked by long-term changes, the first differences of the  $b$  residuals ( $m$  eliminated) were correlated with the corresponding pH difference series. No relationship was apparent, however, except for the control series. Here a coefficient of 0.556 was obtained, but this, in view of the selection involved and the lack of independence of the difference series, cannot be said to reach a significant level.

With regard to the fluctuations of actinomyces and fungi, neither show the same clear-cut relationship with moisture. The most prominent feature of the fungi series is, however, a tendency to rise throughout the period, and this bears a certain resemblance to the temperature (moisture eliminated) trend. The real significance of this trend, especially as no relationship with moisture was observed, must clearly remain a matter of doubt. It will be noticed that the partial regression coefficient of  $f$  on  $m$  appears significant, the slight resemblance of the fungi to the moisture series being brought out only when the trend effect mentioned above had been partly eliminated in terms of the variate  $t$ .

For actinomyces, the association appears equally divided between moisture and temperature. This again implies no more than the general similarity to the moisture or temperature trend, but the change in shape of the trend on the irrigated and unirrigated plots recalls the bacterial association with moisture and renders at least plausible the assumption of a real relationship of numbers of actinomyces with moisture. To investigate further the slight apparent association of  $a$  with pH, short-term fluctuations were examined by means of differences as for bacteria. The only apparent association was for the irrigated plots not receiving nitrogen, but even here  $r$  was only 0.336 and not significant. The slight relationship observed in table 1 has, therefore, been assumed to be arising spuriously from a trend effect, and has not been regarded as real.

With regard to the correlations between the dependent variates, it will be noticed that the negative correlation between bacteria and fungi is increased after elimination of the effects of moisture and temperature. This accords with Jensen's results (16). It will be noticed also that there is evidence of a simple positive correlation between bacteria and actinomyces, but this is reduced after elimination of temperature and moisture effects. Apart from the fact that Jensen also obtained a significant positive partial correlation between bacteria and actinomyces, the result receives some additional support from the fact that the simple and partial correlations are both positive, even though the method used to obtain the figures for  $b$  for dates subsequent to May 10 (that is, by subtracting from the total count the actinomyces count on the same plates) would tend to produce an inverse relationship.

Thus, to sum up, it is claimed that for the data examined, a clear-cut rela-

tionship exists between bacterial numbers, as shown by plate counts, and the moisture content of the soil. A similar, though somewhat less well-established, relationship appears to exist between the numbers of actinomyces and the moisture content, but a similar relationship in the case of fungi appears doubtful. For bacteria, no effect of temperature was observed which could not be fully accounted for in terms of moisture. For actinomyces and fungi the relationship is more obscure. There is no evidence that the pH of the soil, within the admittedly limited range experienced in this work (6.1 to 6.8), has exercised any effect on numbers of bacteria, actinomyces, or fungi. There is some slight evidence of a positive correlation between numbers of bacteria and actinomyces even after the effects of moisture and temperature (if any) have been eliminated, and in spite of the fact that errors in the method of obtaining the data tended to produce an opposite effect. Finally, there is some evidence of a negative correlation between bacteria and fungi.

#### DISCUSSION

The study of the causes underlying the variations in numbers of micro-organisms has engaged the attention of numerous workers, but opinions have been by no means unanimous regarding any positive effects of moisture and temperature. There appears to be some measure of agreement, however, that temperature has relatively little effect. That organic matter is of overriding importance is, of course, clearly established, but in one and the same soil the change in the total amount of organic matter present during a season is of a much smaller order of magnitude than that which occurs between soils in different fields with different agricultural histories. Nevertheless, small changes in the amount or quality of a small fraction of the total organic matter may exert an important influence.

A review of the literature concerning the influence of moisture and temperature on numbers of soil organisms reveals the fact that little definite information has been obtained. Some conclusions that have been drawn do not bear careful scrutiny and under some circumstances have been unjustified and even invalid. Some observers have obviously ignored the fact that merely to demonstrate a correlation between two variables does not necessarily establish a causal relationship between them. Fabricius and von Feilitzen (13) claimed to show that the numbers of bacteria in a peat soil were influenced by temperature, but the paucity of the data leaves the matter open to doubt on statistical grounds. Engberding (12), working on soils on which various agricultural crops were growing, records a positive correlation between soil moisture and bacterial numbers, but it is doubtful whether the figures he gives reach a suitably high level of significance. He concluded that soil temperature had very little, if any, effect on numbers. Conn (4) records a correlation between total numbers of bacteria plus actinomyces and moisture in two soil plots, but his conclusion also is weakened by the fact that the data are not susceptible to statistical treatment. In 1916 Waksman (24) recorded his inability to show

any correlation between bacterial numbers and moisture or temperature; subsequently (25) he claimed to show a relationship between bacterial numbers and soil moisture content; the data as published, however, are too few to permit adequate statistical treatment. Crump made weekly counts in 1916-17, and found that bacterial numbers and moisture content varied directly much more frequently than they varied inversely. In 1922 Cutler, Crump, and Sandon (7), who were probably the first to realize the necessity for frequent and sustained observations, collected data every day for a year, but in spite of the abundance of their data, they were unable to satisfy themselves that any definite connection existed between the variations they observed in *fallow arable soil* and changes in such factors as temperature, moisture, or rainfall. They obtained, however, very convincing evidence of an inverse relationship, subsequently confirmed by Telegdy-Kováts (21), between numbers of bacteria and active amoebae. Referring to their work in a more recent publication (6), Cutler and Crump conclude that "the observed seasonal changes in numbers are due to an inherent urge in the spring and late autumn." No definite conclusions in respect of the effect of temperature and moisture can be drawn from the results of Smith and Worden (19), although the fluctuations which they observed were subsequently shown to be significant by Thornton and Fisher (22). Thornton and Gray (23) were also unable to trace any connection between bacterial numbers and moisture or temperature in arable soil, although they were able to demonstrate in one instance a parallelism between bacterial numbers and rainfall. In 1932 Cobb (3) recorded low numbers during drought, from which she inferred a causal relationship, but her data, which referred to forest soil, were far too few to permit adequate statistical treatment. Jensen (16) concludes that a "strong positive correlation existed between moisture content and numbers of bacteria, and a similar, though less well-pronounced, correlation between moisture and numbers of fungi, whereas the numbers of actinomyces did not seem to be influenced by changes in the moisture content." He goes on to say that "none of these groups of organisms showed any actual correlation with the temperature or any definite seasonal changes apart from those resulting from changes in moisture." His data, which consisted of about 50 observations collected at irregular intervals during 1931-1933 from the same pasture field in the grounds of Sydney University, were examined statistically by means of partial correlations.

As was shown in the foregoing section dealing with the statistical treatment of the data, very strong evidence of this positive correlation was also found, and there was a suggestion also that numbers of actinomyces and possibly also fungi were related in a similar way to the moisture status of the soil. Thus, as far as bacteria are concerned, the results here described are in agreement with those of Jensen, but contrast sharply with those of Cutler, Crump, and Sandon. It is submitted that the reason for this apparent contradiction is to be found in the fact that whereas the work of Cutler et al. was carried out in bare fallow soil, that is, in the *absence* of surface vegetation, both the work



here described and the work of Jensen were conducted in grassland soil, that is, in the *presence* of surface vegetation. At this point it is convenient to cite the results obtained by Wilson and Lyon, and by Starkey. Wilson and Lyon (27) showed that the numbers of various species of bacteria of such widely different physiological character as ammonifiers, nitrifiers, denitrifiers, and nitrogen fixers, when grown in previously sterilized soil, were very much greater in the presence of maize or timothy plants than in their absence. They concluded that the cause of the stimulation was the excretion of materials from the roots of the plants. Starkey (20) studied the effect of the stage of development of the plant on bacterial numbers, and found that for a large variety of plants, both in the greenhouse and in the field, the numbers of bacteria increased *pari passu* with the development of the plants, the maximum number being found at the period of maximum growth. He noted also that there was a rapid decline in numbers when the plants died. Numbers of actinomyces and filamentous fungi, however, showed little, if any, definite increase. In the light of these results there would appear to be little doubt that the numbers of bacteria in a pasture soil are influenced to a very large extent by the roots of the herbage, and that this influence will vary in proportion with the amount of herbage present. Furthermore, it is now only necessary to postulate that the supply of organic matter from the roots is closely associated with active growth of the herbage in order to arrive at a reasonable explanation of all the observed facts. It is suggested therefore that *the seasonal changes in temperature and moisture are not the direct cause of the seasonal changes in numbers of bacteria, but that in controlling the growth of the surface vegetation, these climatic factors control the amount of energy material reaching the bacteria as root excretions and also, in all probability, in the form of material sloughing away from the roots in the course of their development.* Presumably Cutler and co-workers and also Thornton and Gray found difficulty in correlating soil moisture content with changes in the level of numbers of bacteria because those changes in moisture content were unaccompanied by corresponding changes in the amount of energy material reaching the bacteria. In the experiments here described the increases in numbers of bacteria during irrigation were due, in all probability, not so much to the increase in moisture *qua* moisture, as to the increased supply of energy material reaching the bacteria as a consequence of the increased growth of the herbage which that moisture produced.

#### *Evidence from other sources*

Apart from the evidence already presented, further support is provided by the results of such work as has been done in other parts of the world under different climatic conditions from those obtaining in the British Isles. The only record of frequent and sustained observations conducted under tropical conditions is that given by Corbet (5), who made weekly counts of the numbers of bacteria and fungi in Malayan forest soils. The numbers he obtained were constant within narrow limits all the year round. The soil

moisture contents, under the conditions of his experience, were almost constant, and the soil temperature varied from 78 to 80°F. As might be anticipated from the considerations already outlined, he found no seasonal changes in numbers corresponding to those observed in temperate climates. The only detailed data of this nature forthcoming from the Southern Hemisphere, so far as the author is aware, are those already referred to, which were collected by Jensen from the pasture soil in New South Wales. On the basis of the suggestions put forward earlier, it may be inferred from the fact that the winters are considerably milder at Sydney, N. S. W., than anywhere in the British Isles, in consequence of which the grass barely stops growing during this time of the year, that the winter depression in numbers of bacteria would be much more restricted in duration and less pronounced, the tendency being thus to produce one winter peak. The figures given by Jensen certainly support this suggestion for the portion of the year which they cover. It should be noted (table 4) that 40 of his 50 counts were taken during the months August to December; consequently they cannot be expected to give information concerning the full range of any seasonal changes.

TABLE 4

*Mean numbers of bacteria in grassland soils for various months [after Jensen (16)]*

	WINTER			SPRING			SUMMER		
	June	July	August	September	October	November	December	January	February
Number of bacteria . . . . .	.....	15	20	18.5	10.5	17.5	12.5	7.7	13.7
Number of observations . . . . .	.....	3	6	8	6	13	7	4	3

Similar considerations would lead one to expect that in some northerly latitudes, for example, in Finland, where grass production is more concentrated into the relatively shorter summer and where summer drought is more unusual and a longer winter is customary, the bacterial numbers would vary correspondingly, the two spring and autumn peaks which are experienced in England being resolved more or less into one summer peak. Unfortunately, no relevant data are forthcoming from Finland or any other country similarly placed with respect to climate.

#### *Seasonal fluctuations in number of organisms other than bacteria*

Numbers of many other types of soil organisms have been found to vary in a similar way according to the season. For example, Bodenheimer and Reich (2) have recorded seasonal fluctuations in numbers of protozoa in Palestine soils. Francé (14) claims that soil algae behave in a similar way. Periodicity of a like nature in the numbers of some fresh-water and marine organisms has been recorded from time to time (1, 8, 9, 15, 18, 26), and Dügelli (10) has shown that in Swiss pastures even the number of worms varies in the same way.

*The soil food-chain*

An exceedingly involved food-chain undoubtedly exists in the soil, and consequently it is most likely that a change in level of numbers of bacteria will bring about corresponding changes in the numbers of other organisms which may be vitally dependent on the bacteria directly or indirectly. The connection between bacteria and amoebae has already been mentioned, and by inference a whole host of similar relationships must exist, for it is only on such a basis that a state of biological equilibrium can be understood. It may be mentioned, parenthetically, that the inverse relationship between bacteria and amoebae, noted by Cutler and his co-workers, is a short-term relationship and not a long-term seasonal change. There is nothing inconsistent in the idea that a long-term direct relationship should be superimposed on a short-term inverse relationship.

*Types of rhythmical behavior of organisms*

The types of rhythmical behavior to which Cutler and Crump refer are not peculiar to microorganisms, but occur throughout the whole range of biology, and may be broadly classified as follows:

1. Changes occurring within an individual organism as a result of some force acting from within it.
2. Changes in a group of like organisms as a result of their action upon one another.
3. Changes in a group of organisms as a result of interaction with a rival or predatory species of organism.
4. Changes in the whole population of a species of organism resulting from changes in the incidence or intensity of purely external factors such as climate and food supply.

Although the existence of rhythmical behavior of organisms such as would be included in class 1 cannot be called into doubt, it would appear to be extremely unlikely that such phenomena would have any effect on the total numbers of organisms present, since there is no reason to expect the behavior of all the individuals to be in phase. If their behavior were observed to be in phase, it could be argued with considerable justification that their concerted behavior must result from the operation of some factor or factors external to the population as a whole, in which case the phenomenon could no longer be regarded as coming within the scope of class 1. The periodic ovulation of human beings, one of the examples quoted by Cutler and Crump, clearly falls into class 1, and on the basis of the foregoing argument can hardly be admitted as evidence of his contention. Furthermore, since it is only the type of rhythmical behavior covered by class 1 which can be most nearly described as "inherent" or "innate," it is submitted that the statements made by Cutler and Crump that "an inherent urge in the spring and the late autumn, . . . causes an increase in vital activity," and that "there is in protoplasm an innate capacity to behave rhythmically," contain no explanation and are no more than restatements of the problem.

There is, however, another type of rhythm which might be regarded as having some effect, namely, the phenomenon of impressed rhythm, where the organism continues to act rhythmically after the primary external factor causing the rhythm has ceased to operate. The well-known behavior of the two Turbellarian worms *Convoluta roscoffensis* and *C. paradoxa* is a case in point. These marine organisms adjust certain of their habits in a rhythmical way, which is in phase with the rise and fall of the tides, and Keeble (17) has shown that they continue to do so for a period of seven or eight tides when kept in the laboratory under suitable conditions of illumination. In the first place, this is a rhythm which is obviously due, under natural conditions, to the influence of an external factor, namely, the tides, however obscure the actual mechanism may be. The secondary effect, the impressed rhythm, is little understood, but in any case it seems in the highest degree improbable that rhythms of this description can be held to account for *seasonal* variations in bacterial numbers, since they are the property of each individual organism, and are not, so far as is known, transmitted through successive generations, as it would be necessary to postulate in the case of bacteria. Thus, it would appear that the long-term seasonal fluctuations in numbers of bacteria may be regarded almost certainly as having their origins in one or other of the factors listed in the three remaining classes. The observed fluctuations are unquestionably the resultant of several factors, some of which may be obscure or may operate indirectly; but however complicated the relationship may be, that they will be found in the last resort to be due to factors external to the organism, and not to causes resident within the living cell, appears equally certain.

The types of change covered by class 2 are usually of the logarithmic increase and decrease type, and refer to the behavior of a whole colony of like organisms. They arise essentially from local conditions of food and environment, the number of viable organisms increasing as conditions are favorable and decreasing with the exhaustion of vital necessities and the possible accumulation of staling products. Since a fluctuation in numbers composing one colony in one part of the soil cannot be linked to similar changes taking place in other colonies of similar organisms in other parts of the soil except through the operation of some external factor affecting all colonies alike, in which case the phenomenon should rightly come in class 4, the fluctuations in the various colonies must be regarded as being essentially out of phase. For this reason it is suggested that this type of fluctuation is also extremely unlikely to find expression as a seasonal variation in numbers.

The third type of fluctuation is that arising from the operation of the various factors inseparably connected with the state of dynamic equilibrium which exists between the various competing animal and vegetable soil forms. The inverse relationship which was demonstrated by Cutler, Crump, and Sandon to exist between active amoebae and bacteria, comes definitely within this class. Although in all likelihood it is one of the prime causes of short-term

variations, it would appear extremely doubtful whether the causes of the seasonal fluctuations can be assumed to arise in any way from such relationships. Even if the increase in bacterial numbers were to be associated with the periodic appearance of some relatively longer-lived organisms, such as worms, it is pertinent then to enquire why they should also appear at these times.

*It is concluded that whereas short-term variations in numbers of microorganisms undoubtedly arise from what may be called competition factors, the long-term changes in numbers are the reflection of the seasonal changes in climatic conditions as affecting the supply of energy material to the microorganisms. Since this energy can become available to the heterotrophic organisms only via the medium of the green vegetation, their growth and activity should be closely associated with the growth and activity of the herbage. The available evidence certainly supports this view and suggests that the difficulty in tracing the seasonal changes in bare fallow soil is due to the absence of any marked increase in numbers of heterotrophic organisms at the appropriate seasons as a result of the bare fallow conditions, where the income of energy material to the soil system is restricted to that supplied by green algae or other small plants which may be able to survive bare fallow conditions.*

#### SUMMARY

Weekly variations in numbers of bacteria, actinomyces, and fungi occurring in grassland soil have been examined in relation to changes in soil moisture content, soil temperature, and soil reaction. Statistical analysis has indicated a strong positive association between numbers of bacteria, as shown by plate counts, and the moisture status of the soil. Not only was this relationship apparent in untreated soil as a result of natural variations in soil moisture, but irrigation during the summer months also significantly increased the numbers of bacteria. A similar, though less well-established, relationship appeared to exist between the soil moisture content and the numbers of actinomyces and fungi. Between the limits experienced, soil temperature and soil reaction appeared to exert no measurable influence on numbers of organisms. It is suggested that the seasonal changes in moisture and temperature are not the direct causes of the seasonal changes in numbers of bacteria, but that in controlling the growth of the herbage, these climatic factors control the amount of energy material reaching the microorganisms in the form of root excretions or sloughed-off root material. Thus, in grassland soils the long-term changes in the numbers of microorganisms are closely associated with the amount and growth activity of the surface vegetation.

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# THE EFFECT OF MOISTURE CHANGES ON SOIL AS A MEDIUM FOR BACTERIAL GROWTH<sup>1</sup>

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In a publication of 10 years ago (1) in which *Bacterium globiforme* was described, it was shown that two soils of low productivity would not support the growth of this organism unless furnished with available carbon and nitrogen sources. In the conclusion of this 1928 paper the following statement was made:

The fact that these two soils lack all necessary carbon and nitrogen compounds to support the growth of *Bact. globiforme* is not improbably associated with their relatively low productivity. It is not suggested that this organism is necessary for the good growth of plants, but rather that general crops cannot thrive in a soil deficient in the substances required for the nutrition of *Bact. globiforme*.

Such a statement as this naturally suggested that the organism might be regarded as an indicator of productivity of a soil and gave rise to the understanding in numerous quarters that it was being thus used at the New York State Agricultural Experiment Station. As a matter of fact, no work with the organism has gone this far, as further investigations showed that the relationship between this organism and availability of soil nutrients was far from simple in nature.

Thus it was shown later (3) that the growth of the organism could be stimulated in some soils by the addition of a considerable variety of nonnitrogenous salts. It was concluded, "The only reasonable explanation seems to be that each of the salts having this stimulating effect has its influence because in some way it frees some nutrient element already in the soil but in unavailable form." If this were the case, the complex nature of the factors affecting the availability of the nutrients of this organism in soil became quite evident.

It was noticed, nevertheless, that stimulation of growth was most frequently observed following the addition of phosphates and potassium salts. It was felt, therefore, that these salts might serve directly as nutrients and that response of the organism to the addition of one of these salts in any particular soil might indicate deficiency of either potassium or phosphorus in that soil.

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Inasmuch as bacteriologists and mycologists have been trying for some time, but without entire success, to devise a quick test for soil deficiencies, it seemed worth while to investigate the possible use of *Bacterium globiforme* for this purpose.

During the investigation, a type of test was devised which has been used for the last 5 or 6 years upon a great variety of soils. Although it has not proved successful for its original purpose (detecting fertilizer deficiencies in soil), it has yielded interesting information as to the behavior of certain bacteria in soil.

#### METHODS

Details of the test are as follows:

Each soil employed in this work was carefully mixed before the test sample was taken. This was sometimes done after complete air drying of the soil, and at other times while the soil was still damp but not so wet as to puddle.

Four 10-gm. lots of the soil were weighed out, and each was mixed with certain ingredients. All lots of the soil were supplied with uniform quantities of glucose, as the source of carbon and energy, and of  $\text{CaCO}_3$ , to neutralize acids produced. In addition to this they were furnished  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{HPO}_4$ , and  $(\text{NH}_4)_2\text{HPO}_4$  in such combinations that one lot contained added N, P, and K; one lacked P; one lacked K; and one lacked both P and K. After preliminary experiments to determine the optimum amounts, the following quantities of these ingredients were added, respectively, to each of the four 10-gm. portions of the soil:

1.  $(\text{NH}_4)_2\text{HPO}_4$ , 0.03 gm. +  $(\text{NH}_4)_2\text{SO}_4$ , 0.03 gm. (lacking K); weight of  $\text{NH}_4$ : 0.0164 gm.
2.  $(\text{NH}_4)_2\text{SO}_4$ , 0.05 gm. alone (lacking K and P); weight of  $\text{NH}_4$ : 0.0136 gm.
3.  $(\text{NH}_4)_2\text{SO}_4$ , 0.05 gm. +  $\text{K}_2\text{SO}_4$ , 0.03 gm. (lacking P); weight of  $\text{NH}_4$ : 0.0136 gm.
4.  $(\text{NH}_4)_2\text{HPO}_4$ , 0.03 gm. +  $\text{K}_2\text{SO}_4$ , 0.03 gm. (complete); weight of  $\text{NH}_4$ : 0.0082 gm.

It will be noticed that none of the above combinations lack nitrogen. This is because preliminary work with soils furnished with only  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{HPO}_4$ , showed such uniformly low counts that they were of no value for comparative purposes. It will also be seen that the amount of N furnished (as  $\text{NH}_4$ ) varies considerably. This is because the optimum quantity in the form of the phosphate proved, for some reason, to be smaller than that in the form of the sulfate.

After these ingredients were mixed with the soil, each portion was placed in a test tube. If the soil was air dry, 1 cc. of distilled water was added to it; but if the soil was moist, no water was added at this point. The tubes were plugged and sterilized in an autoclave for 1 hour at 15 pounds pressure.

The culture for inoculation had meanwhile been prepared by growing for 24 hours, at  $30^\circ\text{C}$ ., on the surface of a slanted tube of beef-extract-peptone agar (in the case of *Bact. radiobacter*, this agar contained 0.2 per cent glucose). After the soil tubes were sterilized, the growth on the agar slant was rubbed up

in sterile water, and a definite amount of the suspension was transferred to the tube. If the amount of moisture in the soil *before* sterilization was 35 per cent of the water-holding capacity of the soil, 1 cc. of inoculum was added. If the soil was drier or wetter than this, the amount of inoculum was increased or decreased so as to make the final moisture conditions approximately uniform. (It was not found possible, unfortunately, to make the moisture conditions absolutely uniform, because the extent of the deflocculation due to the heating was so variable that the final water-holding capacity of the sterilized soil varied in an unpredictable way.)

The inoculated tubes were incubated 7 days at 30°C. (This temperature and the length of incubation were selected after considerable preliminary investigation to find how soon and under what conditions the bacteria attained their highest numbers.) The numbers of organisms in the soil were then counted by the microscopic method previously described (2). This method, in brief, is to suspend 0.5 gm. of soil in 4.5 cc. 0.015 per cent gelatin, to smear 0.01 cc. of the suspension over a measured area on a slide, and to stain with rose bengal solution (1 per cent in 5 per cent phenol with the addition of 0.01–0.02 per cent  $\text{CaCO}_3$ ).

#### SEARCH FOR A SATISFACTORY TEST ORGANISM

As has been indicated, the use of *Bact. globiforme* did not prove a satisfactory indicator of nutrient deficiencies in the soil, although some of the early tests were promising. Investigations by the same method were, accordingly, begun with a number of other soil bacteria, mostly of the non-spore-forming, slow-liquefying group. No organism so promising as the first one investigated was discovered until work was undertaken with *Bact. radiobacter*, Löhnis.

The latter organism seemed at the beginning to show such striking responses to the influence of different soils and of the ingredients added to them that most of the remaining work was carried on with it. Table 1 is given here chiefly to show that these variations can be considerable and that there may be a certain degree of correlation between the counts attained by the organism and the productivity of the soil. The most striking points brought out in this table are as follows: The low counts with the first soil (which is not under cultivation); the very low counts of the second soil unless furnished either potassium or phosphorus; the striking response to phosphorus in the case of the third soil; and the very slight response to either potassium or phosphorus in the case of the last two soils. These four observations agree in a general way with the productivity of the soils, and fairly good agreement occurred upon repetition of the tests.

After this apparent correlation was found, some hundreds of determinations were made in hopes of demonstrating that the degree of response shown by this organism to such nutrient elements in several soils was proportional to the response shown by certain crops when grown in these same soils as indicated by greenhouse and field experiments. The hopes of using the tests in this way,

TABLE 1

*Seven-day counts of Bacterium radiobacter in soils supplied with glucose and  $\text{CaCO}_3$  plus certain mineral salts; then sterilized and inoculated—moisture content before sterilization not controlled*

Figures indicate millions per 0.5 gm. of dry soil

	MINERAL SALTS ADDED*			
	$(\text{NH}_4)_2\text{HPO}_4$ $(\text{NH}_4)_2\text{SO}_4$ (lacking K)	$(\text{NH}_4)_2\text{SO}_4$ (lacking K and P)	$(\text{NH}_4)_2\text{SO}_4$ $\text{K}_2\text{SO}_4$ (lacking P)	$(\text{NH}_4)_2\text{HPO}_4$ $\text{K}_2\text{SO}_4$ (complete)
A marshy woodland soil.....	290	500	1,030	870†
A rather poor soil, especially deficient in K and P.....	1,120	390	1,230	1,380
A highly productive soil somewhat deficient in P.....	1,620	760	920	2,260
Two moderately productive soils responding chiefly to N fertilization	2,000	1,540	1,610	3,400
	1,770	1,540	1,740	2,780

\* See "Methods."

† This count was made in soil given complete nutrients but in the form of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{K}_2\text{HPO}_4$ .

TABLE 2

*Counts of Bact. radiobacter in a single lot of air-dry soil (VSI), made by the same technic as that in table 1*

Figures indicate millions per 0.5 gm. of dry soil

DATE	MINERAL SALTS ADDED*			
	$(\text{NH}_4)_2\text{HPO}_4$ $(\text{NH}_4)_2\text{SO}_4$ (lacking K)	$(\text{NH}_4)_2\text{SO}_4$ (lacking K and P)	$(\text{NH}_4)_2\text{SO}_4$ $\text{K}_2\text{SO}_4$ (lacking P)	$(\text{NH}_4)_2\text{HPO}_4$ $\text{K}_2\text{SO}_4$ (complete)
May 1, 1934.....	2,030		2,070	1,670
Oct. 25, 1934.....		650		2,120
Jan. 7, 1935.....	990	265	375	1,195
Jan. 7, 1935.....	1,165	545	515	1,480
Feb. 4, 1935.....	615	205	350	1,205
Feb. 4, 1935.....	690	340	390	1,090
Feb. 4, 1935.....	900	240	535	1,025
Dec. 5, 1935.....	1,085	530	560	1,655
Dec. 5, 1935.....	695	430	560	1,375
Dec. 5, 1935.....	1,975	530	430	1,865
Dec. 5, 1935.....	1,180	385		1,580
June 2, 1937.....	1,350	860	1,120	1,755

\* See "Methods."

however, did not prove to be justified. It was soon discovered that some factor or factors operated to cause irregularities in the numbers which the organism could attain in any soil.

Table 2 illustrates such a case. All the tests shown in this table were made with one soil of rather low productivity—Volusia silt loam from the Bare Hill

area west of Rushville, N. Y. It will be seen that the highest counts were obtained in the first two determinations. The data suggest that under optimum conditions this organism can attain a count of at least two billions per gram, provided the proper nutrients are added, but that in all but the first two tests some factor or factors prevented it from reaching these maximum numbers.

What could this factor be? The first suggestion, naturally, was that the culture had lost vigor when the later tests given in this table were made. Various methods of invigorating were tried, sometimes with moderate success and sometimes with none. It was finally concluded that too frequent transfers of a culture on artificial media decreased its ability to attain high numbers in soil, and that it was well, therefore, after every few months of work to go back to the stock culture and thus to obtain a strain that had not been so recently transferred on a fresh medium. Beyond this, no effort to invigorate the culture proved successful. Even under the best of conditions, there was plainly some factor other than the vigor of the culture which often operated to prevent its developing to maximum numbers.

#### EFFECT OF MOISTURE CHANGES

The first clue as to what this factor might be was obtained by noticing that soils in which it was impossible to obtain counts much over one billion were samples that had been kept for some time in air-dry condition. It began to be suspected that, in some way, keeping the soil in such a condition injured it as a medium for the bacteria under investigation. A preliminary experiment or two was planned, therefore, in which some of a soil giving low counts was kept moist for a few weeks before the tests were made. The results were interesting because when this moistened soil was mixed with the usual ingredients and inoculated, the counts obtained with complete nutrients were about twice as high as those that had been obtained when the air-dry soil was used. Accordingly, a more carefully controlled experiment was planned. In this experiment five soil samples were employed as follows:

VS1, the same lot of Volusia silt loam from Bare Hill employed in the earlier work (table 2).

H7 and H7b, two samples of Honeoye stony loam taken at different times from the same spot a few miles northwest of Phelps, N. Y.

P1, a sample of Plymouth sandy loam from near the shore of Long Island Sound, taken at Cold Spring Harbor, Long Island, N. Y.

VST1, a sample of Volusia stony silt loam taken from the Turkey Hill section, east of Ithaca, N. Y. Although similar in many respects to VS1, it showed much more tendency to puddle and to cake upon wetting.

The moisture-holding capacity of each soil was determined. Then four lots of each soil were prepared in duplicate—one kept air dry; the second moistened to 25 per cent of its water-holding capacity and kept in a tumbler covered with a Petri dish top; a third, similarly watered to 35 per cent; and a fourth, to 45 per cent of the water-holding capacity. These moistened soils were weighed

every few days, and the water that had been lost by evaporation was restored. At the end of 1 week, 2 weeks, and 3 weeks, respectively, 10-gm. samples of the various soils were mixed with glucose,  $\text{CaCO}_3$ , and the aforementioned combination No. 4 of mineral salts (containing N, P, and K). Each 10-gm. portion was placed in a test tube (1 cc. of water added to the air-dry soil). These tubes were then sterilized as usual; and one set was inoculated with *Bact. globiforme*,

TABLE 3

*Seven-day counts in soils held at controlled moisture levels\*; then supplied with complete nutrients,† sterilized, and inoculated*

Figures indicate millions per 0.5 gm. of dry soil

SOIL‡	ORGANISM	AIR- DRY SOIL	HELD AT 25 PER CENT OF WATER-HOLDING CAPACITY, FOR			HELD AT 35 PER CENT OF WATER-HOLDING CAPACITY, FOR			HELD AT 45 PER CENT OF WATER-HOLDING CAPACITY, FOR			AVER- AGE
			1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks	
VS1	<i>radiobacter</i>	1,400	1,315	1,820	2,105	1,760	2,120	2,115	1,355	1,920	1,835	1,775
	<i>globiforme</i>	1,755	1,850	1,150	1,890	3,020	1,800	2,245	1,725	2,200	1,540	1,918
H7	<i>radiobacter</i>	1,335	1,715	1,740	1,515	1,665	2,090	2,125	1,345	2,280	1,955	1,777
	<i>globiforme</i>	1,050	1,735	1,225	1,620	2,170	1,400	1,685	1,750	1,670	2,040	1,635
H7b	<i>radiobacter</i>	1,278	2,090	2,360	2,178	2,068	2,478	2,260	2,113	2,495	2,318	2,164
	<i>globiforme</i>	1,160	1,795	2,028	2,183	2,253	2,503	2,365	2,100	2,103	2,530	2,102
P1	<i>radiobacter</i>	1,695	1,760	1,805	2,105	2,158	2,060	2,210	1,750	1,950	1,825	1,932
	<i>globiforme</i>	1,743	1,803	1,670	1,490	1,998	2,053	2,225	1,700	1,893	1,933	1,851
VST1	<i>radiobacter</i>	1,583	1,758	1,613	2,203	2,240	1,945	2,418	2,318	2,120	2,053	2,025
	<i>globiforme</i>	1,163	1,890	1,815	2,128	2,138	2,035	2,058	2,308	2,333	2,455	2,032
Treatment averages...		1,416	1,771	1,723	1,942	2,147	2,048	2,171	1,846	2,096	2,049	1,921
Aver. for	<i>radiobacter</i>	1,458	1,728	1,868	2,021	1,978	2,139	2,225	1,776	2,153	1,997	1,934
	<i>globiforme</i>	1,374	1,815	1,578	1,862	2,316	1,958	2,116	1,917	2,040	2,100	1,907

\* The moisture treatment varied only *before* sterilization and reinoculation. The final moisture content of all the tubes was about 50 per cent of water-holding capacity.

† See "Methods."

‡ VS1, Volusia silt loam from Bare Hill; H7 and H7b, two samples of Honeoye stony loam; P1, a sample of Plymouth stony loam from Cold Spring Harbor; VST1, Volusia stony silt loam from Turkey Hill.

the other, with *Bact. radiobacter*, the bacterial growth being suspended in varying amounts of water so as to make the final moisture content of the different lots of soil comparable. The tubes were then incubated, and counts were made as usual on the seventh day.

This experiment was too large to handle when all the tests were made simultaneously. The soil samples for this purpose, accordingly, were set up at

various times during a period of about 3 months. The results are summarized in table 3.

The work with soil VS1 was performed first and showed that this soil, with which high counts had not been obtained for some time, could be converted again into a good medium for the growth of the test organisms by proper moisture treatment preceding sterilization and reinoculation. The later tests with the other four samples tended to verify the results with VS1. The averages for the various moisture treatments, as given in the last three rows of the table, show a very marked improvement for the entire experiment when the soils were held at 35 per cent of their moisture-holding capacity for 1 to 3 weeks, almost as much improvement at the 45 per cent level, and some improve-

TABLE 4

*Analysis of variance of counts given in table 3, from air-dry soil and the soils held for 3 weeks at varying moisture levels*

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES OF DEVIATIONS*	MEAN SQUARE*	RATIO OF MEAN SQUARE TO ERROR (F)	COMMENT
Total.....	39	6.2993			
Between means of					
soils.....	4	0.6851	0.1713	2.21	To be significant <i>F</i> should be greater than 3.26
organisms....	1	0.0391	0.0391	0.503	To be significant <i>F</i> should be greater than 4.75
moisture levels.....	3	3.3129	1.1043	14.2	Any value of <i>F</i> over 5.95 is <i>highly</i> significant
Interactions:					
soil-organisms.....	4	0.0501	0.0125		
moisture-organisms....	3	0.0997	0.0332		
moisture-soils.....	12	1.1627	0.0969		
Remainder (error).....	12	0.9587	0.0779		

\* The counts given in table 3 were converted to billions (decimal point moved 3 places farther to the left) before these computations were made.

ment at the 25 per cent level. The improvement apparently took place slowly at the 25 per cent level, continuing, in fact, for the whole 3 weeks of the experiment; whereas at the 35 per cent level there was no further improvement after the end of the first week.

It is also noticeable from table 3 that two of the soil samples, namely VST1 and H7b, showed almost uniformly higher counts than did any of the other samples. Brief inspection of the table does not show, however, whether these differences were of any significance. It is striking that the highest and the lowest averages were obtained, respectively, with H7b and H7, the two samples obtained from exactly the same spot in the field; this certainly suggests that the differences between soils are not significant.

Another point of interest is that the final averages for *Bacterium radiobacter* and *Bacterium globiforme*, respectively, were almost exactly the same. This observation, together with the fact that low counts of one organism usually paired with low counts of the other, and *vice versa*, suggests that both of these organisms behave about the same in the soils studied and under the conditions of this experiment.

Although these conclusions seemed fairly reliable, it was not regarded as safe to trust them without statistical analysis of the data. These were, accordingly, analyzed for variance by the method outlined by Snedecor (4). The results are given in table 4. In this table the values of  $F$  given in the fifth column are striking. The value of  $F$  for the soils is almost, but not quite, high enough to be significant; that for the organisms is not only too small to be significant but so low that it can be virtually disregarded; whereas that for the moisture levels ( $F = 14.2$ ) is more than twice as high as the value 5.95, which would be *highly* significant. From these values it was reasoned that the conclusions given in the preceding paragraphs are justified, that is, the moisture level of the soil before sterilization and reinoculation has a very decided effect on results, the differences between the soils are not great enough to be significant, and the two organisms employed seem to behave in exactly the same manner.

The similarity between the results obtained with the two organisms is regarded as very important. It seems to indicate reliability of this method of comparing soil treatments. Although not all the differences observed can yet be explained, it is felt that they are real differences, and that present inability to interpret some of them is due to lack of understanding of all the factors involved.

#### A POSSIBLE EXPLANATION

The effects of varying moisture levels in the soils were a little surprising and seemed at first somewhat difficult to explain. If the final moisture content of the soil in the culture tubes had varied, the explanation would be simple; but since it was kept as constant as possible, the explanation evidently must be more complex. Apparently in some way a soil that has been kept in air-dry condition may become a less favorable medium for the growth of these organisms than the same soil that has been kept moist for 2 or 3 weeks before sterilization and addition of the nutrients necessary to support the bacteria. Only two possible explanations have occurred to the writers:

1. When a soil is kept moist for 2 or 3 weeks, the bacteria therein must, obviously, be more active than when it is in an air-dry condition. Possibly they produce growth-accessory substances or in other ways render the soil more suitable for the bacteria subsequently inoculated into it than when kept in an air-dry condition.

2. Volk (5) has shown that alternate wetting and drying of soils treated with soluble potassium salts causes rapid fixation of the potassium in a nonreplaceable form. It is entirely possible, therefore, that some such phenomenon might occur under the conditions of this experiment. Keeping the soil air-dry for a considerable period may fix the potash, or some

other necessary base present in the soil, to such an extent that the regular quantities of nutrients added to the culture tubes in this experiment were insufficient to permit maximum growth of the bacteria. It is, of course, also possible that the condition of the colloids in the soil after standing for some time in an air-dry condition might be such that not only the potassium already present in the soil, but that added to the culture tubes in the experiment, might be fixed.

The data reported in table 5 were obtained in the course of a series of experiments to determine which of these two explanations seemed the more probable. In these experiments, three soil treatments, as follows, were compared: One consisted of keeping the soil unsterilized and air-dry; the second, of bringing it up to 35 per cent of its water-holding capacity and maintaining it at this moisture level without sterilization for 3 weeks; the third, of adding to it the same amount of water as in the second treatment, but of sterilizing it in the autoclave and keeping it in cotton-stoppered flasks. Soil given the third treatment was divided into two portions, each in a separate flask, one of which was opened after 2 weeks, the second after three weeks; this was to prevent contamination of the portion tested the third week when the 2-week test was made.

Two soil samples were employed in this series of experiments, sample VS1 in the first seven experiments, and sample VST1 in the last three. After the samples had been kept moistened for the requisite length of time, they were mixed with the usual amounts of glucose and calcium carbonate and with varying quantities of  $K_2SO_4$  and  $(NH_4)_2HPO_4$ . In the third and fourth columns of table 5 the quantities of these last two chemicals are given, the figures in bold-face type indicating the quantities that were above the standard amounts employed in the preceding work.

In planning this experiment it was realized, of course, that sterilization not only would prevent bacterial growth but might produce physical and chemical changes in the soil and consequently that it would not prove a perfect control on the effect of bacterial activities. Whether from this cause or some other factor, these experiments did, as a matter of fact, prove inconclusive. The counts obtained in the soil that had been moistened and then sterilized were usually higher than those in the soil that had been kept air-dry, but they were rarely as high as those in the soil which had been moistened but not sterilized; they did not come so near to equalling the latter counts in soil VST1 as they did in soil VS1. This suggests that part of the explanation of the higher counts in the moistened soil may be the effect of the bacteria that grow in it during the period when it is kept moist, but because there was no way of separating the bacterial effects from the physical and chemical action of the heat, this conclusion is not well established.

Those tests which were planned to show whether fixation of some base occurred in the air-dry soil were interesting, but likewise inconclusive. In soil VS1 distinctly higher counts were obtained when the quantities of potassium sulfate were increased slightly above the standard amount employed in the previous experiments. In some instances the counts obtained with twice the



standard quantity of this salt almost equalled those obtained in the unsterilized moistened soil. With soil VST1, the same tendency was observed, but the counts did not come so near to equalling those obtained in the moistened soil.

TABLE 5

*Seven-day counts in soils held at controlled moisture levels, either sterilized or unsterilized, then supplied with varying quantities of salts before inoculation*

Count figures indicate millions per 0.5 gm. of dry soil

EXPERIMENT NUMBER	ORGANISM	NUTRIENTS ADDED TO 10 GM. SOIL (IN ADDITION TO 0.1 GM. GLUCOSE AND 1 GM. $\text{CaCO}_3$ )		COUNTS IN UNSTERILIZED AIR-DRY SOIL		COUNTS IN UN- STERILIZED SOIL HELD AT 35 PER CENT OF WATER- HOLDING CAPAC- ITY, FOR		COUNTS IN STERILIZED SOIL HELD AT 35 PER CENT OF WATER- HOLDING CAPAC- ITY, FOR	
		$\text{K}_2\text{SO}_4$	$(\text{NH}_4)_2\text{HPO}_4$	First test	Second test	2 weeks	3 weeks	2 weeks	3 weeks
		gm.	gm.						
Soil VSI									
1	<i>Radiobacter</i>	0.03	0.03	860	955	1,900	1,820	1,285	1,130
	<i>Globiforme</i>	0.03	0.03	635	1,500	1,310	1,500	1,250	2,027
2	<i>Radiobacter</i>	0.03	0.03	500	1,095	1,610	2,240	905	935
	<i>Globiforme</i>	0.03	0.03	960	895	1,830	1,610	790	1,415
3	<i>Radiobacter</i>	0.03	0.03	1,420	1,385	1,950	2,065		
	<i>Globiforme</i>	0.03	0.03	970	840	1,435	2,620		
4	<i>Globiforme</i>	0.03	0.03	625	1,175	2,215	1,635		
	"	0.06	0.03	880	1,220	1,575	1,340		
	"	0.1	0.03	1,130	1,425	1,670	1,385		
	"	0.03	0.06	1,100	800	1,465	1,245		
	"	0.03	0.1	700	720	750	1,390		
5	<i>Globiforme</i>	0.03	0.03	935	990	2,045	1,990		
	"	0.06	0.03	1,120	1,225	2,305	1,660		
	"	0.1	0.03	1,635	1,320	1,450	1,810		
	"	0.15	0.03	1,515	1,065	1,215	1,160		
	"	0.20	0.03	1,065	1,005	1,135	1,690		
	"	0.03	0.06	1,685	1,570	1,245	1,385		
6	"	0.03	0.1	1,335	1,360	1,530	1,790		
	<i>Globiforme</i>	0.03	0.03	1,090	1,105	2,510	1,980	1,585	1,910
	"	0.06	0.03	1,710	2,005			2,060	1,255
	"	0.1	0.03	1,240	1,285			1,990	950
7	"	0.15	0.03	1,305	1,190			1,680	755
	<i>Globiforme</i>	0.03	0.03	1,260	1,235	2,415	2,120	1,475	1,480
	"	0.06	0.03	1,810	1,680			1,875	1,710
	"	0.1	0.03	1,545	1,510			2,235	1,240
	"	0.15	0.03	1,305	1,360			1,575	1,100

TABLE 5—*Concluded*

EXPERIMENT NUMBER	ORGANISM	NUTRIENTS ADDED TO 10 GM. SOIL (IN ADDITION TO 0.1 GM. GLUCOSE AND 1 GM. CaCO <sub>3</sub> )		COUNTS IN UNSTERILIZED AIR-DRY SOIL		COUNTS IN UN- STERILIZED SOIL HELD AT 35 PER CENT OF WATER- HOLDING CAPAC- ITY, FOR		COUNTS IN STERILIZED SOIL HELD AT 35 PER CENT OF WATER- HOLDING CAPAC- ITY, FOR	
		K <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> - HPO <sub>4</sub>	First test	Second test	2 weeks	3 weeks	2 weeks	3 weeks
		gm.	gm.						
Soil VST1									
8	<i>Radiobacter</i>	0.03	0.03	970	1,080	2,140	1,685	1,095	1,220
	"	0.06	0.03	1,170	1,165	1,930	1,675	1,770	1,175
	"	0.10	0.03	1,225	1,560	1,925	1,715	1,250	1,050
	"	0.06	0.06	1,170	995	1,775	1,220	1,070	935
	"	0.03	0.06	1,220	1,285	1,800	1,545	1,245	1,060
	"	0.03	0.10	1,240	1,200	1,760	1,315	1,190	1,060
9	<i>Radiobacter</i>	0.03	0.03	795	655	1,790	1,070	1,070	910
	"	0.06	0.03	1,050	965	2,145	1,200	955	980
	"	0.10	0.03	1,085	1,230	1,595	1,650	890	780
	"	0.06	0.06	900	780	1,340	1,080	835	785
	"	0.03	0.06	1,040	945	1,720	1,300	825	870
	"	0.03	0.10	1,060	860	1,585	1,185	820	970
10	<i>Radiobacter</i>	0.03	0.03	815	1,320	1,070	2,110	670	1,210
	"	0.06	0.03	810	1,640	955	2,015	720	1,320
	"	0.10	0.03	1,085	1,655	890	2,020	800	1,150
	"	0.06	0.06	825	1,455	835	1,990	505	960
	"	0.03	0.06	945	1,665	825	2,005	675	1,150
	"	0.03	0.10	805	1,490	820	1,990	520	1,030

Increasing the amount of ammonium phosphate, however, proved as apt to decrease as to increase the counts.

This would seem to indicate that the addition of increasing amounts of potassium sulfate to the air-dry soil improves it, at least up to a certain point, for the growth of bacteria. In the moistened soil, however, the effect was quite different. The same quantities of additional potassium sulfate which seemed to improve the air-dry soil, were very apt to have a depressing effect on the count in the moistened soil. The results, however, were too irregular to allow any very definite conclusion.

They suggest, nevertheless, that there is a delicate balance of nutrients in soil which may easily be upset by some change in the colloidal complex, fixation of potassium possibly being one factor involved. Apparently the quantities of potassium sulfate and ammonium phosphate which were employed regularly in the experiments reported in table 3 were optimum, ordinarily, for the bacteria in question when these salts were added to soil that had been kept at 35 per cent of its moisture-holding capacity for 2 or possibly 3 weeks. Under

such conditions increasing the quantity of salts added usually decreases the count obtained. If, however, because of drying of the soil, sterilization, or too long holding in a moist condition, considerable of the potassium, or possibly some other base, becomes fixed, the amounts of salts regularly added in this work are insufficient to produce maximum counts; and increases in numbers of the bacteria can, therefore, be obtained by increasing the quantities added. Most noticeable results were obtained in these experiments by increasing the quantities of potassium sulfate. This suggests that potassium is the critical element; but it does not prove the case, because the phenomenon of base exchange may take place, and consequently adding this salt might increase the availability of some other cation.

Whatever the explanation, it is very clear from these later experiments, as well as from those reported in table 2, that the soil is a better medium for the growth of these bacteria if it has been kept moist for a period of about 2 weeks. Such results go far to explain the difficulties encountered in trying to use this type of bacteriological procedure as a test for nutrient deficiency in soil. It is difficult to compare plant nutrition with that of microorganisms. Plants live through many changes in weather and accordingly in the moisture level of the soil in which they are growing. If, as the present results seem to indicate, such changes impair or improve the soil as a place for growth, possibly by fixing or liberating necessary nutrient elements, the consequences are naturally less serious to higher plants than to microorganisms which have a short life period and are accordingly more strongly affected by the conditions which obtain during that brief period. This may well explain one of the factors which underlies the difficulties encountered by soil biologists who have been trying to devise tests for this purpose, whether the test organism be a bacterium, a yeast, or a mold. It is certain, at least, that in the present instance the great fluctuations in counts obtained when the nutrients supplied were not varied indicate the operation of some factor which makes such a procedure of dubious value as a test for nutrient deficiencies.

#### SUMMARY

The experiments reported in this paper were begun in an effort to study nutrient deficiencies of soils by the use of either *Bacterium radiobacter* or *Bact. globiforme* as the test organism. Growth of the test organism in tubes of sterilized soil, with varying nutrient elements added, was determined by a microscopic count 7 days after inoculation.

Although the method has not yet proved useful for the purpose originally intended, it did bring out certain points of considerable interest; to wit:

Almost identical results were obtained with the two test organisms whenever they were directly compared. This seemed to indicate that the test is dependable, and that the differences it brings out are real differences, even though it is not yet possible in every case to explain them on the basis of treatment or soil conditions.

Minor differences were observed between the various soils studied, but statistical analysis proved these differences too small to be significant.

The soil samples studied (five in number), if allowed to become air dry, were impaired as media for growth of the test organisms, even after they were brought up to optimum moisture content and the necessary nutrients added to support bacterial growth.

It proved possible to restore air-dry soil to its normal condition in this respect by holding it at 35 per cent of its water-holding capacity for about 2 weeks before adding the bacterial nutrients, sterilizing, and inoculating with the test organisms.

Experiments were carried on to show whether the improvement of the soil after moistening might be due to changes brought about in it by growth of the natural soil flora during the 2-week period while the soil was moist, or by release during this period of bases that might possibly have been fixed by the soil colloids while the soil was in an air-dry condition. Indications were obtained that fixation of potassium might be one of the factors involved; but results varied too greatly to be conclusive.

Changes in the condition of the nutrients due to variations in the moisture level may well be more serious to bacteria, studied for a week or so after inoculation, than to plants which live months, usually through many changes in moisture conditions. This may explain one of the difficulties encountered in using microorganisms to indicate plant nutrient deficiencies.

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# THE CHEMICAL COMPOSITION OF SOIL FROM CULTIVATED LAND AND FROM LAND ABANDONED TO GRASS AND WEEDS<sup>1</sup>

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Reference has been made in previous publications (2, 5, 6) to the fact that it is when land goes under the plow that deterioration begins. The unbroken prairie or land abandoned to natural grasses and weeds may not change very much in chemical composition over a long period of years. There is, however, a fair probability that it may gain slightly, especially in content of nitrogen and organic matter.

When the soil fertility plots were laid out at the New Jersey Agricultural Experiment Station in 1908, provision was made for eight 1/20-acre plots, one-half of each plot to be continuously in a 5-year rotation (corn, oats, wheat, and 2 years of timothy), the other half to be abandoned to grass and weeds (2). The fertilizer and lime treatment for these plots were to be the same for both sections. The plan has been adhered to to date with only slight exception. By 1923, dewberry vines were overrunning some of the plots of the uncultivated section, and for this reason it seemed best to plow them under. Corn was grown on all the plots of this section for the one season only. No other crops have been removed. Some years the growth of weeds and grasses has been allowed to stand; more often it has been clipped with the mowing machine and allowed to lie on the ground, the next year's growth coming up through the dead material.

The fertilizer combinations used on these plots were as follows:

<i>Plot number</i>	<i>Fertilizers</i>
57 and 58	P and K
59 and 60	N and K
61 and 62	N and P
63 and 64	N, P, and K

Originally, the nitrogen was supplied in the form of ground fish at the rate of 600 pounds per acre. Later, the nitrogen was supplied in the form of a mixture of nitrate of soda and sulfate of ammonia to give a total of 51 pounds of nitrogen per acre (half the nitrogen from nitrate of soda and half from sul-

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

fate of ammonia). Superphosphate was originally applied at the rate of 600 pounds per acre; and muriate of potash, at the rate of 300 pounds per acre. These amounts were later reduced to 300 pounds and 150 pounds respectively. Lime in the carbonate form has been added from time to time to maintain the pH at about 6.0-6.5.

The purpose of this paper is to show the changes that have occurred in the chemical composition of these soils over a period of 30 years, with especial reference to certain total constituents and changes in certain physicochemical properties.

#### EXPERIMENTAL

In July 1937, soil samples were collected from these plots for chemical analysis. The surface samples were taken to a depth of 6 $\frac{1}{2}$  inches and the subsurface samples from 6 $\frac{1}{2}$ -12 inches. In addition four plots from the uncultivated section were sampled at successive 2-inch depths down to 6 inches.

The total nitrogen, phosphoric acid, and potash were determined by A. O. A. C. methods (1). The carbon content of the 1937 samples was determined by the wet combustion method of Tiurin (11). The cation exchange capacity was determined by the barium acetate method (8). The exchangeable calcium, magnesium, and potassium were displaced from the soils either by the normal ammonium acetate method or by electro dialysis (9), and these cations were determined in the extracts by the usual methods (1). Exchangeable hydrogen was calculated by subtracting the sum of the exchangeable calcium, magnesium, and potash from the total cation exchange capacity.

The pH of samples as taken (field pH) and ultimate pH values were determined by the glass electrode on 1-1 soil suspensions.

#### CHANGES IN NITROGEN AND CARBON CONTENT OF CULTIVATED AND UNCULTIVATED SOILS OVER A 30-YEAR PERIOD

Table 1 gives the results of nitrogen and carbon determinations made on samples from the cultivated and uncultivated sections of plots 57 to 64 in 1913, 1916, and 1937. This table brings out the fact that, without exception, both nitrogen and carbon are now higher in the uncultivated section than in the cultivated.

The average difference between the two sections in nitrogen content of the nitrogen-treated plots, was 0.02 per cent in 1913, 0.023 per cent in 1916, and 0.067 per cent in 1937. In pounds of nitrogen per acre 6 $\frac{1}{2}$  inches (2,000,000 pounds of soil), these values would correspond to 400, 460, and 1,340 pounds respectively. The average nitrogen difference between the cultivated and the uncultivated sections of the plots that receive no nitrogen was 0.012 per cent in 1913, 0.026 per cent in 1916, and 0.039 per cent in 1937. These values correspond to 240, 520, and 780 pounds of nitrogen to the acre respectively.

The results are in accord with previously published data (3, 4) showing that liberal applications of phosphorus, potassium, and calcium favor the appear-

ance of volunteer leguminous plants on abandoned land and also the fixation of atmospheric nitrogen by nonsymbiotic bacteria, consequences which no doubt account for the fact that on the uncultivated sections of these plots the nitrogen supply is fairly well maintained. Volunteer leguminous plants, especially clovers, also appeared in the no-nitrogen plots of the cultivated section following timothy or grain, but their presence did not appreciably influence the nitrogen content of the soil. Scarcely any volunteer legumes appeared on the nitrogen-treated plots of the cultivated section.

On the basis of an average of all the nitrogen-treated plots, the cultivated section shows slightly less nitrogen in 1916 than in 1913 and still less in 1937, in spite of the fact that the plots have received fair annual applications of nitrogenous fertilizers. For the uncultivated section, the average is the same in 1913 and 1916, but a gain of 0.039 per cent by 1937 is noted.

TABLE 1  
*Nitrogen and carbon in soil, 1913, 1916, and 1937*

TREATMENT	CULTIVATED SECTION						UNCULTIVATED SECTION					
	Nitrogen			Carbon			Nitrogen			Carbon		
	1913	1916	1937	1913	1916	1937	1913	1916	1937	1913	1916	1937
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
P and K . . . . .	0.085	0.073	0.077	1.012	0.999	0.975	0.097	0.099	0.116	1.225	1.272	1.529
N and K . . . . .	0.086	0.081	0.081	1.095	1.067	0.967	0.099	0.102	0.155	1.272	1.306	1.906
N and P . . . . .	0.084	0.081	0.070	0.997	0.979	0.863	0.107	0.106	0.146	1.352	1.382	1.848
N, P, and K . . . .	0.084	0.083	0.080	1.035	1.062	0.975	0.108	0.107	0.132	1.323	1.334	1.696
Average of N-treated plots.	0.085	0.082	0.077	1.042	1.036	0.935	0.105	0.105	0.144	1.316	1.341	1.817

It is evident that the total carbon is being gradually decreased on the cultivated section. This is shown by an average percentage of 1.042 in 1913, 1.036 in 1916, and 0.935 in 1937. It is further emphasized by the fact that determinations made on samples collected in 1909 from nearby plots, where the soil is the same as the soil of the plots under consideration, show 1.21 per cent of total carbon (2). From this it would appear that the cultivated plots have lost 0.17 per cent during the period from 1909 to 1916 and 0.275 per cent during the period from 1909 to 1937. On the other hand, the carbon is increasing in the uncultivated plots as is shown by an average of 1.316 per cent in 1913, 1.341 per cent in 1916, and 1.817 per cent in 1937. Thus, it would appear that during the period 1909 to 1916 the carbon content of the uncultivated soils has increased by about 0.13 per cent, which would be equivalent to slightly more than  $1\frac{1}{4}$  tons of carbon per acre. During the period from 1909 to 1937 the carbon content has increased by 0.607 per cent, which would be equivalent to about 6 tons of carbon per acre. The gains and losses in nitrogen and carbon content are shown graphically in figures 1 and 2.



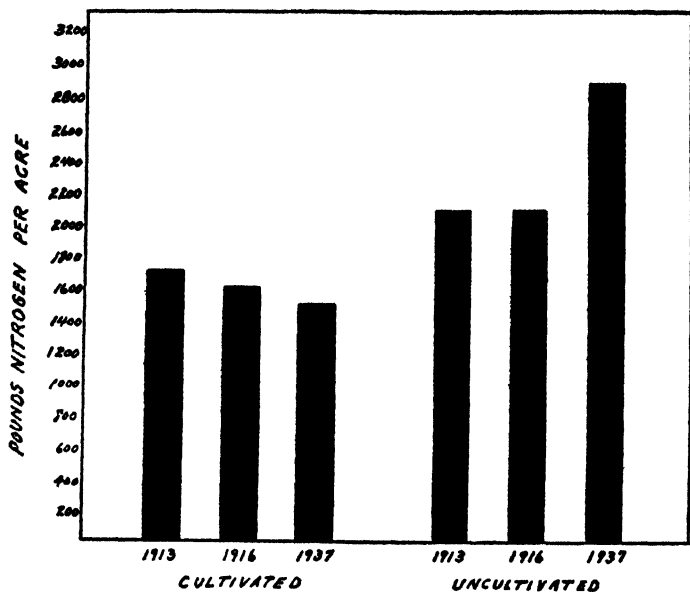


FIG. 1. NITROGEN IN CULTIVATED AND UNCULTIVATED SOILS AT DIFFERENT PERIODS

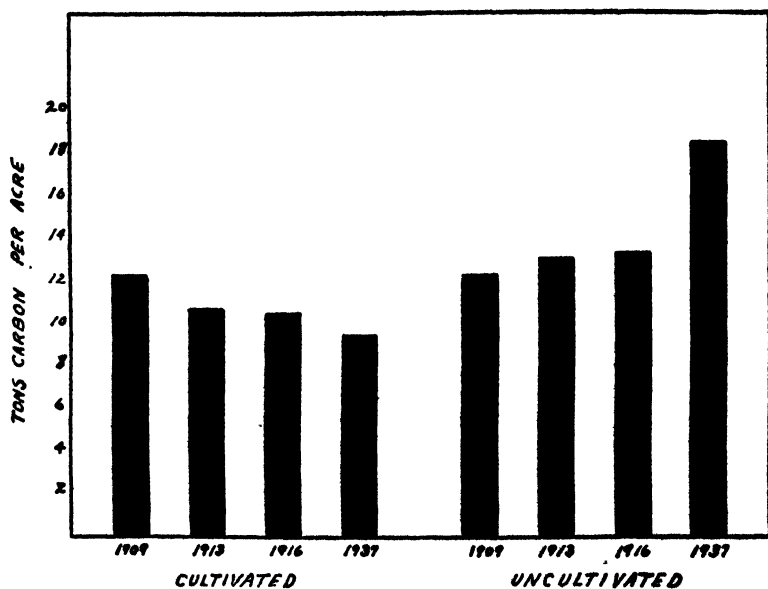


FIG. 2. CARBON IN CULTIVATED AND UNCULTIVATED SOILS AT DIFFERENT PERIODS

Table 2 shows the total nitrogen, carbon, phosphoric acid, and potash content of the surface soils for 1937 in comparison with these same constituents for the subsurface soils. It will be noted that the nitrogen and carbon con-

tent is lower for the subsurface soils than for the surface soils. Also the subsurface soils of the uncultivated section contain higher amounts of nitrogen and carbon than do the subsurface soils of the cultivated section. The total nitrogen and carbon content of both surface and subsurface soils of the uncultivated section is decidedly higher on the nitrogen-treated plots than on the no-nitrogen plots, but this does not hold true for the cultivated section.

### *Phosphoric acid and potash content*

The surface soils of both sections of the plots contain more  $P_2O_5$  than do the subsurface soils, undoubtedly because the major portion of soluble phosphates is fixed in the surface layer of soil (3). The plots that have received no phosphorus application are considerably lower in this constituent than are the other

TABLE 2  
*Analysis of soils collected in 1937 from cultivated and uncultivated plots*

TREATMENT	CULTIVATED SECTION					UNCULTIVATED SECTION				
	pH	N	$P_2O_5$	$K_2O$	C	pH	N	$P_2O_5$	$K_2O$	C
		per cent	per cent	per cent	per cent		per cent	per cent	per cent	per cent
<i>Surface soils</i>										
P and K . . . . .	5.92	0.077	0.119	0.99	0.98	6.38	0.116	0.123	1.11	1.53
N and K . . . . .	5.49	0.081	0.070	0.80	0.97	6.01	0.155	0.069	1.11	1.91
N and P . . . . .	5.71	0.070	0.120	0.87	0.86	6.01	0.146	0.169	1.18	1.85
N, P, and K . . . .	5.79	0.080	0.131	1.17	0.98	6.29	0.132	0.156	1.16	1.70
<i>Subsurface soils</i>										
P and K . . . . .	6.39	0.046	0.041	1.16	0.52	6.89	0.059	0.052	1.24	0.73
N and K . . . . .	6.44	0.040	0.056	1.12	0.47	6.62	0.071	0.046	1.26	0.83
N and P . . . . .	6.35	0.045	0.077	1.13	0.50	6.67	0.080	0.090	1.27	0.92
N, P, and K . . . .	6.50	0.049	0.083	1.13	0.53	6.83	0.069	0.084	1.16	0.85

plots. Soil from the phosphate-treated plots of the uncultivated section also shows a higher percentage of phosphoric acid than does soil from the corresponding plots of the cultivated section. This is no doubt due to the fact that on the uncultivated plots the crop residues are returned to the soil, whereas considerable  $P_2O_5$  is removed in the crops grown on the cultivated section, and also because the loss through leaching is greater on the cultivated section.

The subsurface soils of both sections contain slightly more total potash than do the surface soils. This seems to be a characteristic of the soils of this region. The plots that receive no potash show, in most cases, just as high a percentage of this constituent as do the plots which receive potash, and in some cases even a higher percentage. This fact indicates that the normal potash content of the soil is high enough to mask the effect of applied potash, and, further, that there is little tendency for potash to accumulate in the soil.

It will be noted in tables 4 and 5, however, that the exchangeable potash is much lower on the plots receiving no potash treatment. The uncultivated section contains slightly more total potash than does the cultivated section. This may be due to the removal of some potash by the crops on the cultivated section and to greater losses through leaching.

*Distribution of some soil constituents at different depths in the uncultivated plots*

The data reported in table 3 were obtained from samples taken at depths of 0-2, 2-4, and 4-6 inches on the uncultivated plots. The pH values, which

TABLE 3  
*Distribution of some soil constituents at different depths in the uncultivated plots*

TREATMENT	DEPTH	pH	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	C
	<i>inches</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
P and K .....	0-2	5.78	0.169	0.201	1.209	2.266
P and K .....	2-4	6.15	0.124	0.164	1.217	1.592
P and K .....	4-6	6.30	0.102	0.139	1.198	1.214
Average .....			0.132	0.168	1.208	1.691
N and K .....	0-2	5.62	0.172	0.100	1.054	2.338
N and K .....	2-4	5.88	0.121	0.073	1.101	1.439
N and K .....	4-6	6.25	0.102	0.059	1.112	1.299
Average .....			0.132	0.077	1.089	1.692
N and P .....	0-2	5.22	0.193	0.195	1.450	2.573
N and P .....	2-4	6.07	0.123	0.156	1.306	1.480
N and P .....	4-6	6.50	0.095	0.122	1.380	1.194
Average .....			0.137	0.158	1.379	1.749
N, P, and K .....	0-2	5.77	0.184	0.171	1.116	2.409
N, P, and K .....	2-4	6.23	0.116	0.156	1.016	1.481
N, P, and K .....	4-6	6.40	0.100	0.140	1.116	1.189
Average .....			0.133	0.156 <sup>a</sup>	1.083	1.693

range from 5.22 to 6.50, increase progressively in each 2-inch layer. The higher pH values at the lower depth are undoubtedly due to the higher base saturation, which is reported in table 4.

The total nitrogen, carbon, and phosphoric acid, all progressively decrease with depth. The phosphoric acid tends to be fixed in the top 2-inch layer. The excess of the other constituents in the top 2 inches is due to an accumulation of the organic material. The plots receiving no phosphates show only about half as much P<sub>2</sub>O<sub>5</sub> as do the other plots. Plots that receive no potash contain more total potash in the soil than do those that receive potash, a fact to which reference has already been made.

*Comparison of the nature of the exchange complex in cultivated and uncultivated soils*

The next phase of this investigation centers around certain changes which might be expected in the nature of the exchange complex existing in the soils of the uncultivated plots. The most important changes which might be looked for in this connection would be increases in the cation exchange capacity, and reductions in ultimate pH brought about by the variation in the ratio of the inorganic exchange complex to the organic exchange complex. The effect of the increase in the organic exchange complex can be evaluated by comparing the exchange capacities of the cultivated soils with those of the uncultivated soils.

TABLE 4

*Distribution of exchangeable cations at different depths in the uncultivated plots*

TREATMENT	DEPTH	pH	ULTIMATE pH	CATION EX- CHANGE CAPAC- ITY	UN- SATU- RATION	EXCHANGEABLE CATIONS				ELEC- TRO- DIALYZ- ABLE P <sub>2</sub> O <sub>5</sub>
						H	Ca	Mg	K	
	<i>inches</i>			<i>m. e. per 100</i>	<i>per cent</i>	<i>m. e. per 100</i>	<i>m. e. per 100</i>	<i>m. e. per 100</i>	<i>m. e. per 100</i>	<i>m. e. per 100</i>
P and K . . . . .	0-2	5.78	3.92	11.46	36.7	4.21	5.91	0.48	0.86	4.37
P and K . . . . .	2-4	6.15	4.06	9.90	30.2	2.99	5.94	0.41	0.56	3.23
P and K . . . . .	4-6	6.30	4.09	8.36	32.9	2.75	4.53	0.44	0.64	2.10
N and K . . . . .	0-2	5.62	3.85	9.72	71.1	6.91	2.84	0.42	0.55	0.49
N and K . . . . .	2-4	5.88	4.03	7.57	37.1	2.81	3.54	0.31	0.91	0.35
N and K . . . . .	4-6	6.25	4.13	7.09	37.7	2.67	3.62	0.28	0.52	0.26
N and P . . . . .	0-2	5.22	3.91	12.06	55.2	6.66	4.59	0.51	0.30	4.46
N and P . . . . .	2-4	6.07	4.02	9.36	31.7	2.97	5.79	0.32	0.28	3.14
N and P . . . . .	4-6	6.50	4.15	8.11	22.8	1.85	5.53	0.32	0.41	2.40
N, P, and K . . . . .	0-2	5.77	3.68	11.87	39.7	4.71	6.13	0.42	0.61	4.02
N, P, and K . . . . .	2-4	6.23	4.20	8.98	32.2	2.89	5.27	0.35	0.47	2.90
N, P, and K . . . . .	4-6	6.40	4.23	8.40	26.3	2.21	5.23	0.32	0.64	2.13

In table 4, data are reported for exchangeable bases, cation exchange capacity, unsaturation, and ultimate pH values of soils from the uncultivated section sampled at depths of 0-2, 2-4, and 4-6 inches. In all cases, the top 2-inch samples show a considerably greater cation exchange capacity than do samples from the lower levels. Thus, the top 2-inch sample has an exchange capacity of 11-12 m.e. per 100 gm. of soil, whereas the 4-6-inch sample has an exchange capacity of only a little over 8 m.e. per 100. The accumulation of new acidoid fractions, namely, humus and phosphoric acid, in the upper layers, accounts for this variation. The influence of phosphoric acid in this connection is reflected in a lower cation exchange capacity on the plots which receive no phosphate. The electro-dialyzable phosphorus, shown in the last

column, also bears a relation to these facts, since it is present in largest amount (about 4 m.e. per 100) in the 0-2-inch depth, followed by that in the 2-4-inch depth, and finally by that in the 4-6-inch depth.

The ultimate pH values of these soils at different depths are further supporting evidence for the above reasoning. Thus, it will be noted that the ultimate pH values are lowest for those samples where there is the greatest accumulation of the acidoid fraction, namely, at the 0-2-inch depth. At this depth the ultimate pH values are all below 4.0.

The amount of exchangeable hydrogen and the percentage of unsaturation of these soils are always greatest in the top 2 inches and in most cases decrease progressively at the 2-4-inch and 4-6-inch depths. The decrease in exchangeable hydrogen with increasing depth accounts for the rise in field pH.

The exchangeable calcium does not vary to any significant extent in the different depths studied, on the plots that receive phosphates. On the plots which receive no phosphate, however, only about half as much exchangeable calcium was found as on the plots receiving phosphates. The exchangeable magnesium in these soils varies only slightly with the phosphate treatment. A slightly higher amount of exchangeable magnesium was found, however, in the top 2-inch samples.

The data for exchangeable potash vary significantly only when the plots receiving potash are compared with those receiving none. Approximately half as much exchangeable potash was found in the latter as in the former. This is interesting when compared with the total potash figures for the same plots which indicate a higher total potash content in the plots receiving no potash.

Table 5 presents data on the cation exchange capacity, unsaturation, and exchangeable bases from soils of the cultivated and uncultivated plots for both surface and subsurface samples. The cation exchange capacities of the soils from the cultivated plots are all lower than those from the respective uncultivated plots. This fact, of course, can be attributed mainly to the lower humus content of the soils from the cultivated section where the organic matter has undergone oxidation. The subsurface soils also have lower cation exchange capacities than the surface soils, since the organic matter and phosphoric acid content of these subsurface soils are lower. With one exception, the plots which receive no phosphate are the lowest in cation exchange capacity both in the surface and subsurface soils. This is to be expected, since phosphate is one of the acidoids which bring about an increase in the cation exchange capacity (7, 8).

The surface soils from both sections are decidedly more unsaturated than the subsurface soils, a fact which is further substantiated by the pH values and by the data on exchangeable hydrogen. Furthermore, the surface soils from the cultivated plots are considerably more unsaturated than those from the uncultivated section. The effects of leaching and of removal of bases by the crops on the cultivated section are responsible for this condition. Thus,

it is interesting to note that both exchangeable calcium and magnesium are lower on the cultivated plots than on the uncultivated.<sup>2</sup> The especially low value for exchangeable calcium (1.80 m.e. per 100) on the plot receiving no phosphate (cultivated section) is associated with the low cation exchange capacity of this plot. On the uncultivated section, the exchangeable calcium of this plot has been increased to 4.95 m.e. per 100, because of the increase in the amount of organic exchange complex as indicated by the higher carbon

TABLE 5  
*Exchangeable cations from cultivated and uncultivated plots*

TREATMENT	CULTIVATED SECTION								UNCULTIVATED SECTION							
	pH	Cation exchange capacity	Unsaturation	Exchangeable cations				pH	Cation exchange capacity	Unsaturation	Exchangeable cations					
				H	Ca	Mg	K				H	Ca	Mg	K		
m. e. per 100	per cent	m. e. per 100	m. e. per 100	m. e. per 100	m. e. per 100	m. e. per 100	per cent	m. e. per 100	m. e. per 100	m. e. per 100	m. e. per 100					
Surface soils																
P and K. . . . .	5.92	6.23	45.3	2.87	2.57	0.53	0.26	6.38	8.56	17.3	1.49	5.43	0.88	0.77		
N and K. . . . .	5.49	5.53	49.2	2.49	1.80	0.52	0.20	6.01	9.03	27.0	2.46	4.95	0.86	0.77		
N and P. . . . .	5.71	5.96	39.2	2.34	3.04	0.52	0.07	6.01	10.27	29.0	2.98	5.99	1.01	0.29		
N, P, and K. . . . .	5.79	6.71	55.9	3.74	2.27	0.48	0.22	6.29	9.91	23.0	2.29	5.80	0.95	0.87		
Subsurface soils																
P and K. . . . .	6.39	4.10	17.0	0.67	2.57	0.56	0.30	6.89	5.82	3.7	0.22	4.40	0.60	0.66		
N and K. . . . .	6.44	3.16	6.6	0.21	2.18	0.53	0.24	6.62	5.35	1.5	0.09	3.89	0.67	0.74		
N and P. . . . .	6.35	4.48	29.3	1.30	2.52	0.60	0.05	6.67	6.70	13.9	0.94	4.95	0.60	0.23		
N, P, and K. . . . .	6.50	4.64	10.0	0.46	3.29	0.62	0.26	6.83	6.30	7.0	0.45	3.94	0.70	0.71		

content (see table 2). The new complex, therefore, retains the exchangeable calcium to a greater degree than does the exchange complex on the cultivated section. It is also true that there is less exchangeable calcium removed from the uncultivated section. The subsurface soils have approximately the same amount of exchangeable calcium as do the surface soils in the cultivated section, even though the cation exchange capacity of the former is lower. This fact together with the unsaturation and the pH values indicates a movement of lime to the lower depths.

The exchangeable potash, like the calcium and magnesium, is considerably

<sup>2</sup> The values for exchangeable magnesium reported in table 5 are twice, and in some cases three times, as great as the values reported for corresponding plots in table 4. This may be explained by the fact that the values reported in table 5 were obtained by extraction with normal ammonium acetate, whereas those in table 4 were obtained by electrodialysis. It has been shown (10) that electrodialysis does not remove all the exchangeable magnesium.

less on the cultivated plots than on the uncultivated, and for similar reasons. Again it may be observed that the plots receiving no potash contain only about one-third as much exchangeable potash as do the other plots in the cultivated section. Relatively more exchangeable potash is present in the uncultivated section than in the cultivated section because the retention of potash in the exchange complex has been enhanced by the greater exchange capacity of these plots. Furthermore, but little potash has been removed from this section by crops (only one crop removed).

From the facts presented, one might well infer that land which has been taken out of cultivation and abandoned to natural grasses and weeds gradually gains in fertility mainly through accumulative processes. Although these processes are very slow, the accumulation of organic residues brings about a greater cation exchange capacity for the soils, which if fertilized will then retain more bases in the exchange complex.

#### SUMMARY

Changes in the chemical composition and physicochemical properties of soil from cultivated land and land abandoned to grass and weeds over a period of 30 years are reported.

Samples of soil were collected in 1913, 1916, and 1937. Subsurface samples ( $6\frac{3}{4}$ –12 inches) were taken in 1937, and, in addition, four plots from the uncultivated section were sampled at successive 2-inch depths down to 6 inches.

Total nitrogen and carbon determinations were made on all samples; and, in addition, total phosphoric acid and potash determinations were made on the 1937 samples. Base exchange studies were also carried out on the 1937 surface and subsurface samples and on the special samples collected at depths of 0–2, 2–4, and 4–6 inches.

Without exception, both nitrogen and carbon are now higher in the uncultivated section than in the cultivated. These data are in accord with the view that liberal applications of minerals favor the appearance of volunteer leguminous plants on abandoned land and also the fixation of atmospheric nitrogen by nonsymbiotic bacteria. On the other hand, the cultivated sections show a gradual depletion of their supply of nitrogen and carbon, since there is comparatively little encouragement for volunteer leguminous plants to come in and restore nitrogen losses, and the removal of the crops prevents the maintenance of the organic matter supply.

Although the subsurface soils of both sections show lower percentages of both nitrogen and carbon than do the surface soils, the subsurface soils of the uncultivated section show higher percentages of these elements than do the subsurface soils of the cultivated section.

Where phosphorus and potassium have been applied, soil from the uncultivated section shows a slightly higher percentage of these elements than does soil from the corresponding plots of the cultivated section. In all plots, phos-

phorus is higher in the surface soil than in the subsurface soil, but the reverse is true for potash.

In the uncultivated section, the pH values increase progressively with each 2-inch increase in depth, down to 6 inches; and the total nitrogen, carbon, and phosphoric acid decrease progressively. The higher pH values at the lower depths are attributed to the higher base saturation at these levels. Much of the phosphoric acid was found to be fixed in the top 2-inch layer; the larger amounts of the other constituents found in this layer are due largely to an accumulation of organic matter.

A study was made of the nature of the exchange complex in the cultivated and uncultivated soils. The cation exchange capacity of the uncultivated soils, which was greatest in the top 2 inches, was found to be higher, in every instance, than that of the cultivated soils. The accumulation of the acidoid fraction, namely, humus and phosphoric acid, in the upper layers of the uncultivated section account for this variation. Furthermore, the ultimate pH values are lowest on those soils in which there is the greatest accumulation of the acidoid fraction.

The effect of leaching and of removal of exchangeable bases by cultivation is reflected in the lower amount of exchangeable calcium, magnesium, and potash in the cultivated soils than in the uncultivated soils.

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## ACTION OF HYDROGEN PEROXIDE ON WEATHERED MICA

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It was noted, while a mechanical analysis was being made of a soil from the Mojave desert, California, that the coarse separates of the lower horizons seemed to contain much more mica than did the original soil. The character of the mica also was strikingly different after the mechanical analysis. The dark brown or black particles of the mica were transformed into a golden flaky variety.

Investigation revealed that the change in the mica was due to the hydrogen peroxide treatment given the soil to destroy organic matter before the mechanical analysis was made. Tablets of the dark colored mica were picked out of the weathered granite from which the soil was derived and were treated with a few cubic centimeters of 30 per cent hydrogen peroxide. Immediately the peroxide decomposed around the mica particles. Then gradually the mica began to exfoliate, and in a few minutes a golden flaky mass of thin mica plates was present in suspension, most of the flakes rising to the surface. Plate 1 shows the mica before and after exfoliation. On oven drying, the flakes formed large coherent masses. Pieces of the untreated mica, when heated, expanded considerably. This fact, along with the optical properties and an X-ray analysis of the material, identified it as an altered hydrated mica having some properties of the vermiculites, which are known to have spacing between the plates. It seemed reasonable, therefore, to suppose that the peroxide penetrated the mica plates, that something there caused its decomposition, and that the evolution of the oxygen split apart the plates. Samples of unweathered biotite and muscovite, which have a compact structure, were tested, but they did not react with the peroxide.

About 20 different samples of vermiculites were then obtained from the Mineralogy Division of the National Museum to be tested. Exfoliation with very active decomposition of the peroxide occurred with only two of the samples, both of them varieties of philadelphite; several others caused a slow decomposition of the peroxide with slight exfoliation; but most of them did not react at all.

The philadelphite samples appeared to be somewhat weathered, as did the soil mica, whereas the other vermiculites appeared unweathered. It was suspected, therefore, that some alteration product between the plates acted as a catalyst in the decomposition of the peroxide. As manganese dioxide is a

very active catalyst and as manganese is a common constituent of micas, a test for that element was made. The two samples of philadelphite, the mica from the Mojave desert soil, and two samples of the vermiculites reacting weakly with the peroxide were digested in 4 per cent nitric acid for about an hour on the steam bath. To all appearances the samples were not altered materially by this treatment. Aliquots of the solutions were then tested for manganese. Very strong test for manganese were obtained in the soil mica and in both samples of philadelphite, whereas only a slight test was obtained in the other two vermiculites. The parent material of the Mojave desert soil had a manganese content of 0.07 per cent, and selected pieces of the altered mica contained 0.31 per cent. It seemed clear, then, that it was manganese dioxide between the mica plates which caused the reaction. As further confirmation of this, a sample of weathered mica was obtained from a rock exposure in Rock Creek Park, Washington, D. C. Small pieces of this mica readily broke off when treated with hydrogen peroxide. But the exfoliation was in small particles rather than in complete plates. From these pieces a thin film of manganese dioxide could be scraped from the surface of the mica plates.

It should be mentioned that with some weathered micas and vermiculites, organic matter or other catalysts such as nickel oxide or chromium oxide, may be present between the plates and cause the same reaction. Hydrated ferric oxide, also, is moderately active in decomposing hydrogen peroxide and may be the effective agent in some instances in causing exfoliation.

Alkaline solutions of hydrogen peroxide decompose much more readily than acid solutions. A few drops of ammonium hydroxide added to the vermiculite samples which reacted weakly with the peroxide caused a more vigorous reaction accompanied by exfoliation of the material. A similar acceleration of the reaction was obtained by heating the slightly acid solution.

The following comments may be made in connection with this reaction:

It gives evidence of the presence of manganese dioxide between the plates of some hydrated weathered micas. This suggests the similar occurrence of metallic oxides such as nickel or chromium in altered micas containing these metals. Thus some indication may be obtained concerning the structure of altered micas and the nature of the weathering.

The exfoliation of weathered mica with hydrogen peroxide may provide a simple means of separating the mica from other minerals with which it may occur. The thin flakes can be easily floated off in water while the other minerals sink quickly to the bottom of the vessel. This scheme was used successfully with the coarse fractions of the Mojave desert granite soil.

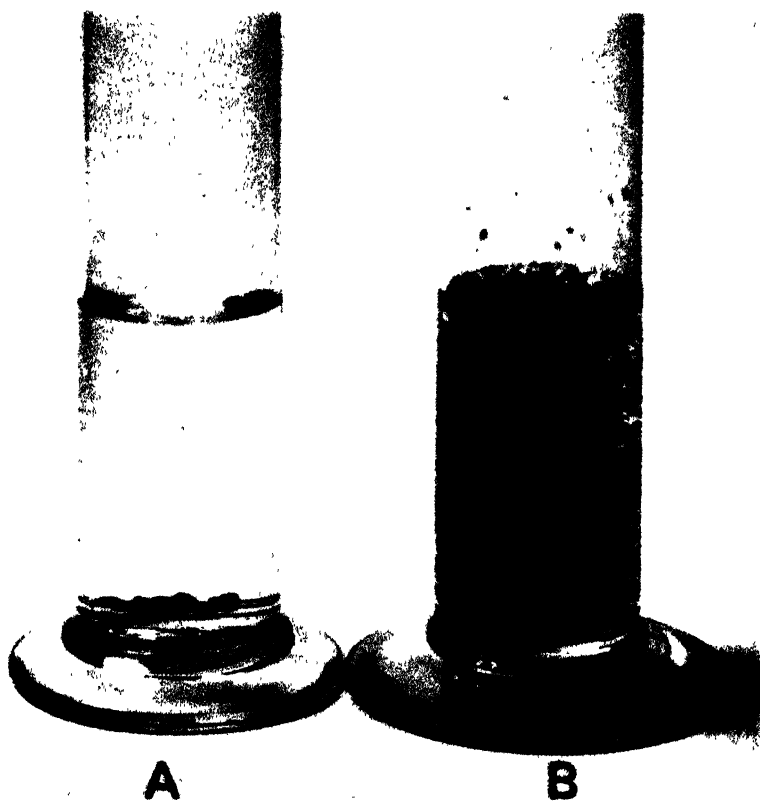
A third consideration is the effect of the peroxide on the mechanical analysis of soils high in mica. Two distinct effects are noted when 6 per cent hydrogen peroxide is used as a pretreatment for removing organic matter in the Bureau of Chemistry and Soils mechanical analysis procedure. In case of a soil containing the hydrated type of weathered mica, treatment with peroxide

resulted in an increase in the coarse separates and a consequent decrease in the finer fractions. This was due to the cohesion of the exfoliated plates of mica when the soil was heated after the peroxide treatment. In case of a soil containing weathered mica not of the hydrated type, the opposite effect was obtained. The hydrogen peroxide tended to break up the larger pieces of mica into smaller flakes, thereby increasing the finer fractions and consequently decreasing the coarser fractions. Significant differences due to the peroxide treatment in the mechanical analysis would be expected only in soils high in mica, especially in the lower horizons where the mica particles are coarser and more abundant.

## PLATE 1

MICA PARTICLES IN WATER COMPARED WITH SIMILAR PARTICLES IN 6 PER CENT HYDROGEN  
PEROXIDE SOLUTION

*A*, untreated pieces of mica; *B*, mica after exfoliation with hydrogen peroxide.





# RAPID DETERMINATION OF ORGANIC CARBON IN SOIL<sup>1</sup>

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The usual procedure for determining organic carbon in soil is to determine total carbon by a combustion method and to deduct from that finding the inorganic carbon, determined separately. This procedure is slow and tedious and requires special apparatus. As far as the author can ascertain, no satisfactory method for determining organic carbon in soil directly has been proposed. A titration method which depends on measurement of the amount of chromic acid reduced by the soil organic matter has been worked out (4), but it seems not to account for all the carbon.

The direct method for determining organic carbon in vegetative plant tissue (3) is so rapid and accurate for carbohydrate and protein material that it was decided to try it on soils. At first it was thought that soil minerals would interfere with the color. Several types of soil were stripped of organic matter, and it was found that the dissolved minerals in strong sulfuric acid did not impart enough color to cause significant off-color tints in the reading of the brown carbon color in a colorimeter. It may be that some soils not tried by the author would give color interference, but it seems unlikely that this would occur in the common soil types. As very few fatty compounds or aromatic compounds not attacked by sulfuric acid are present in soils, the method should be very accurate in determining total organic carbon under usual field conditions.

## PROCEDURE

Heat strongly on a hot plate (not over a free flame) 0.25 to 2 gm. (depending on the carbon content) of soil in 25 cc. of 50 per cent (by volume) sulfuric acid in a 200-cc. Erlenmeyer flask until foaming ceases, white fumes start coming off profusely, and acid just starts to condense on the sides of the flask but not longer than this. Cool, make up to 25 or 50 cc. (depending on the C content) with 50 per cent  $H_2SO_4$ . Shake the solution well, pour into a tall graduate or test-tube, and allow to settle. As soon as the supernatant liquid is clear, compare with the standard in a colorimeter. Some solutions may have to stand overnight to clear sufficiently for satisfactory reading. If it is desired to make immediate reading, a plug of glass wool may be placed in an appropriate funnel and the solution decanted from the soil residue as much

<sup>1</sup> The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the director.



as possible on to the filter. Considerable filtrate should be allowed to run back into the original flask. Pour back until the solution is clear.

#### PREPARATION OF STANDARD

Heat on a hot plate 5 cc. of 0.25 per cent pure anhydrous glucose solution with 25 cc. of 50 per cent (by volume)  $H_2SO_4$  to the same point as that in the soils procedure. Care must be taken not to heat too long, or the standard will be weak. The volume will now be about 15 cc. Cool, and make up to exactly 20 cc. with 50 per cent  $H_2SO_4$ . One cubic centimeter contains 0.25 mgm. of C. If 0.125 mgm. is desired for low C soils, dilute to 40 cc. with 50 per cent  $H_2SO_4$ . The standard should be made up fairly close to the time the unknowns are tested.

TABLE 1  
*Organic carbon, in per cent*

	ALIQUOT	SAMPLE 1	SAMPLE 2
Black silt loam.....	1	3.09	3.06
	2	3.06	3.03
Black silt loam and millet turned under.....	1	3.55	3.47
	2	3.54	3.40
Red clay.....	1	1.25	1.20
	2	1.23	1.18
Soil below sod.....	1	2.23	2.19
Black silt loam and 20 tons of manure per acre.....	1	4.46	4.56
Black silt loam and 40 tons of manure per acre.....	1	6.40	6.41

#### RESULTS

At first several soils were tested to see how the test behaved with different types and in different samplings of the same soil. The results are presented in table 1.

In order to check the method further, additions of known quantities of carbohydrate were used. The results, presented in table 2, show that virtually all the added carbon was recovered.

In order to make certain that all carbon was being determined, samples of soil in which organic carbon had been accurately determined were obtained from the University of Illinois and from the U. S. Department of Agriculture. Table 3 presents these results.

It will be seen from this table that the colorimetric method gave slightly higher results in nearly all cases. An explanation might be that the standard was slightly weak or that it or the soil samples had absorbed moisture. To test this, a U. S. Bureau of Standards sample was dried at 55°C. for several days. The results were the same. Overheating in the acid digestion, of

TABLE 2

*Recovery of added organic carbon in soil*

SAMPLE*	MILLIGRAMS OF CARBON		SAMPLE*	MILLIGRAMS OF CARBON	
	Found	Recovered		Found	Recovered
1 c	19.840	4.96	5 c	19.840	4.96
1	14.880		5	14.880	
2 c	19.230	5.03	6 c	21.185	4.95
2	14.205		6	16.235	
3 c	18.940	4.57	7 c	19.685	4.98
3	14.370		7	14.705	
4 c	25.000	4.84	8 c	19.685	4.98
4	20.160		8	14.705	
1 c R.C.	16.500	4.60	9 c	27.175	4.86
1	11.900		9	22.320	
2 c R.C.	17.100	5.20	10 c	37.000	4.95
2	11.900		10	32.050	

\* 500-mgm. samples of soil were used, except for red clay (R.C.), 1000-mgm. samples of which were used; 5 mgm. of carbon in the form of pure glucose was added to each "c" sample.

TABLE 3

*Comparison of rapid colorimetric method for total carbon with furnace combustion method*

SAMPLE*	TOTAL ORGANIC CARBON		SAMPLE†	TOTAL ORGANIC CARBON	
	Furnace combustion†	Colorimetric		Furnace combustion	Colorimetric
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
13873	3.13	3.20	1. Barnea	0.53	0.54
13876	1.98	2.11	2. Roseworthy	2.91	2.95
13915	2.38	2.42	3. Medemblik	0.80	0.80
14035	1.46	1.66	4. Ohio	17.83	17.99
14076	1.22	1.38	5. Mnyusi	2.72	2.77
13777	4.11	4.31	6. Ohehe	2.74	2.80
13780	1.66	1.72	7. Hungarian	2.36	2.42
14034	2.53	2.55	8. Hungarian		
14052	2.27	2.31	(B horizon)	1.86	1.92
14075	2.35	2.45	9. Iowa	2.07	2.23

\* Furnished by R. H. Bray, agronomy department, University of Illinois; see (1) for description.

† See Winters and Smith (5).

‡ Furnished by H. G. Byers, Bureau of Soils, U. S. Department of Agriculture; see (2) for description.

course, might weaken the standard; but duplicate standards checked, which probably would not be so if this were a source of error. As differences between findings by the two methods are not large, the rapid colorimetric method appears to be fairly accurate. High amounts of sodium chloride in some of the U. S. Department of Agriculture samples did not interfere. In fact, none of the soil extremes tested appeared to cause interference. Some were a little harder to clear than others, but the brown color matched well with the standard in all samples.

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## INTERACTION BETWEEN CARBONATES AND SOILS

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One of the most characteristic reactions of acids is associated with their power of decomposing carbonates with the evolution of  $\text{CO}_2$ . On the other hand, alkali carbonates can decompose alkaline earth salts with the production of insoluble carbonates and the alkali salt of the acid. Carbonates play an important part in soils. The amelioration of acidity by the application of  $\text{CaCO}_3$  and the deterioration resulting from the introduction and accumulation of  $\text{Na}_2\text{CO}_3$  are well known examples of the rôle of carbonates in soils.

Titration curves of alkali carbonates with acids would furnish an excellent method of following these reactions, for the production of  $\text{CO}_2$  could be estimated at every step by determining the pH value of the reaction mixture. This is obvious from the fact that the titration of an alkali carbonate with any acid is equivalent to its titration with  $\text{CO}_2$  up to the formation of bicarbonate. Beyond that stage the bicarbonate begins to decompose, and the characteristic shape of the curve is dependent on the nature of the acid used, for with a strong acid the inflection will be sharper than that with a weak acid; on account of the hydrolysis of the alkali salt. These titration curves would not only furnish information on the decomposition of carbonates but also indicate the strength of the acid.

On the other hand, titration curves of alkali carbonates with alkaline earth salts can give valuable information on the precipitation of insoluble carbonates. Apparently such curves would correspond to the pH values of carbonate solutions of decreasing concentrations until all the carbonate was precipitated, when the pH value would show a sudden drop.

Since carbonates are known to react not only with acid soils but with soils containing exchangeable Ca (2), similar methods of study could be employed as with ordinary acids and soluble Ca-salts. Two types of alkali and alkaline earth carbonates could be studied, of which  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  are typical and generally found in soils.

In the experiments reported in this paper, the following reactions were studied:

Reaction of  $\text{Na}_2\text{CO}_3$  with common soluble acids, with soil acidoid, and with an insoluble acid.

Reaction of  $\text{Na}_2\text{CO}_3$  with calcium salts and with calcium soils.

Reaction of  $\text{CaCO}_3$  with common soluble acids and with soil acidoids.

Reaction of  $\text{CaCO}_3$  with sodium salts and with sodium soils.

Exchangeable bases were removed from soils in the usual way by exhaustive treatment with dilute HCl. From the resulting H-soils, Ca- and Na-soils, were prepared by neutralizing with the corresponding hydroxides.

#### REACTION OF SODIUM CARBONATE WITH ACIDS AND WITH SOIL ACIDOID

Sodium carbonate is the sodium salt of dibasic carbonic acid. Titration with an acid first leads to the formation of the acid salt. The most characteristic feature of this titration is the point of inflection corresponding to the acid salt formation. The stronger the acid used for titration, the more pronounced is this point of inflection. This is shown by the titration curves with various acids and with soil acidoid (fig. 1). It is to be understood, of course, that the soil was used as a whole. Throughout this work no attempt was made to

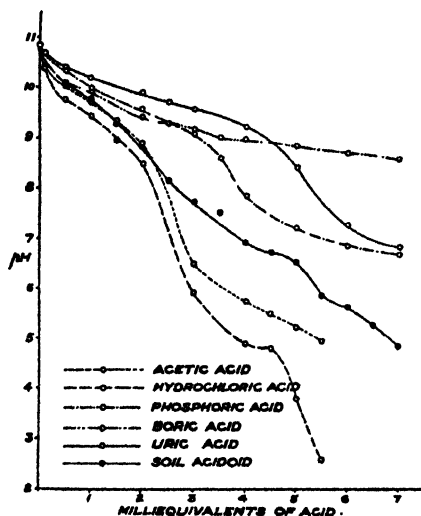


FIG. 1. TITRATION OF SODIUM CARBONATE WITH VARIOUS ACIDS AND WITH SOIL ACIDOID  
( $\text{Na}_2\text{CO}_3 = 5 \text{ me.}$ )

separate the clay fraction, for such a procedure is unnecessary and is likely to confuse the issue. Colloidal acids are so uniformly distributed in the soil that no advantage can be gained by separating them from the inert material. The titration method of determining the equivalent weight of a soil acidoid ( $T/2$ ) has been explained (3). All the incremental additions of soil acidoids or of Ca soil are given, therefore, in milliequivalents; thus, all the results are brought to a uniform basis. Figure 1 shows that the point of inflection corresponding to the bicarbonate formation is as pronounced with the soil acidoid as that with acetic acid or uric acid, and more pronounced than that with boric acid. The case of uric acid requires special mention. This acid is virtually insoluble in water, the solubility being 1:10,000. Since a normal solution could not be made, uric acid was added in the solid state, the exact

amount corresponding to 1 m.e. being weighed for each incremental addition. It would thus appear that the insoluble part of uric acid behaves as an acidoid and gives a titration curve with sodium carbonate as if it were soluble. These results emphasize the fact that the distinction between ordinary acids and soil acidoids is purely arbitrary and merely refers to the differences in their solubility.

#### REACTION OF SODIUM CARBONATE WITH CALCIUM SALTS AND WITH CALCIUM SOILS

Calcium salts react with  $\text{Na}_2\text{CO}_3$ , with the production of  $\text{CaCO}_3$ , which is insoluble. The titration of a  $\text{Na}_2\text{CO}_3$  solution with a calcium salt, therefore, represents the pH value of  $\text{Na}_2\text{CO}_3$  solutions of decreasing concentrations, until the whole is precipitated as  $\text{CaCO}_3$ , when there is a sudden drop in the pH

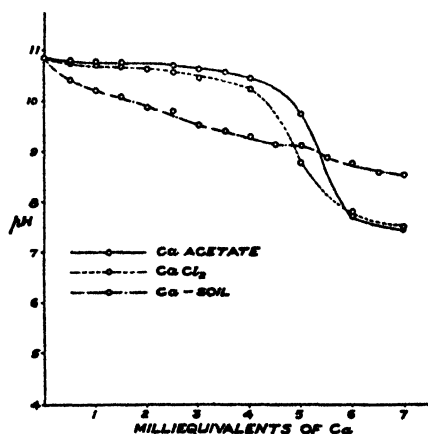


FIG. 2. TITRATION OF SODIUM CARBONATE WITH CALCIUM SALTS AND WITH CALCIUM SOIL  
( $\text{Na}_2\text{CO}_3 = 5$  m.e.)

value. The pH value again shows only a slight change with further additions of Ca salt. The drop corresponding to the precipitation of the entire  $\text{Na}_2\text{CO}_3$  is considerable with neutral salts like  $\text{CaCl}_2$ , it is less with salts of weak acids like Ca acetate, and it may be entirely absent with salts of extremely weak acids. This will be clear from the following considerations: Salts of strong acids like  $\text{CaCl}_2$  or  $\text{NaCl}$  are unbuffered neutral solutions, therefore they take up the pH value of any buffer solution to which they are added. Salts of weak acids, on the other hand, are more buffered than are the neutral salts, and their titration curves with strong bases generally do not show a sharp inflection at the neutral point. The latter also lies at a higher pH value. Sodium carbonate, a salt of a strong base with a weak acid, is thus well buffered. When  $\text{CaCl}_2$  is added to it, the products of reaction are  $\text{CaCO}_3$ , which is insoluble, and  $\text{NaCl}$ , which has very little effect on the reaction, and thus a sharp

inflection is obtained when the whole of the  $\text{Na}_2\text{CO}_3$  has been precipitated as  $\text{CaCO}_3$ . The curves showing the course of reaction between  $\text{Na}_2\text{CO}_3$  and calcium salts and calcium soil are given in figure 2. It is seen that the soil curve is steeper than the salt curves but shows no inflection. The reason for this apparently anomalous behavior is that the pH value of the soil was about 6.5. As this does not correspond to the neutral point, the soil could still react with sodium carbonate (2). The pH value is thus lowered still further until the whole of the sodium carbonate has reacted. The completion of this reaction, however, leaves the soil at a higher pH value than would be the case with a neutral salt. Further additions of the soil amount to adding one buffer solution to another, and the drop in pH, therefore, is comparatively slight.

#### REACTION OF CALCIUM CARBONATE WITH ACIDS AND WITH SOIL ACIDIDS

In view of the abundance of  $\text{CaCO}_3$  in soils and of its use for neutralizing soil acidity, the reaction of  $\text{CaCO}_3$  with acids and with soil acidoids is of particular interest. The well-known reaction



in which  $\text{CaCO}_3$  is decomposed by acids with the production of  $\text{CO}_2$ , unlike the reaction with alkali carbonates, has no point of inflection corresponding to the bicarbonate formation. The very slight solubility of  $\text{CaCO}_3$  in water has an effect on the course of the titration curve similar to the effect of Ca salts on the reaction of a saturated solution of  $\text{CaCO}_3$ , until all the  $\text{CaCO}_3$  is used up. The point at which this occurs will correspond to the inflection of the curve, if the titration is done with a strong acid; the inflection will be less marked with a weak acid and may be entirely absent with an extremely weak acid. The titration curves of  $\text{CaCO}_3$  with common acids and soil acidoids are given in figure 3. It will be seen that the inflection with the soil acidoid is at least as marked as that with acetic acid.

It was of interest to determine the final pH values of acidoids from a number of soils when shaken with excess of  $\text{CaCO}_3$ . For this purpose, 19 soils after the usual acid treatment and leaching were shaken for 1 hour and for 48 hours with excess of  $\text{CaCO}_3$ ; the final pH values were determined by the glass electrode; and the amount of  $\text{CaCO}_3$  decomposed by the soil was estimated by the carbonate-oxalate method of Puri (2). The results are given in table 1. Base exchange capacities of the soils ( $T/2$  values), determined by titration (3) and by ammonia that can react with the soils (4), are also given. It will be noted that 48 hours' shaking is not necessary for the attainment of equilibrium. There is no appreciable increase in the Ca taken up by the soil when shaken longer than 1 hour, though there is a slight fall in the pH values. The general agreement between  $T/2$  values, the ammonia that reacted, and the equilibrium with  $\text{CaCO}_3$  measured under entirely different sets of conditions would leave no doubt that we are dealing in all cases with reactions that are fundamentally

identical. This can be reconciled only with the view that acidoids behave like true acids in their action on carbonates, ammonia, and other alkalies. It is seen that the pH value of soil in equilibrium with  $\text{CaCO}_3$  is approximately equal to 7, in spite of the fact that a saturated solution of  $\text{CaCO}_3$  has a pH value of 8.5. The fact that this value is reduced to 7 in the presence of Ca-soil is of great interest. It is evidently due to the lowering of the dissociation of  $\text{CaCO}_3$  by the presence of a common ion; and the action is similar to that of soluble Ca salts. This will be seen from figure 4, in which the pH values of a saturated solution of  $\text{CaCO}_3$  in the presence of varying amounts of Ca and Na salts and soils are given. The influence of single-base soils is of the same order as that of acetates.

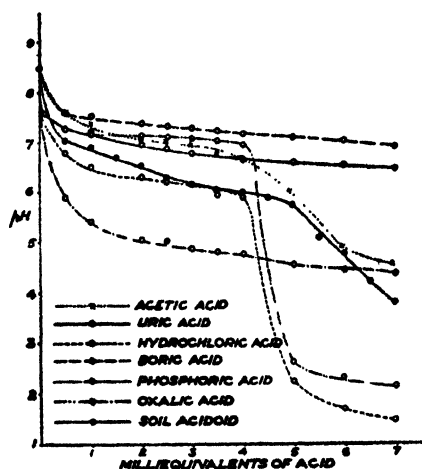


FIG. 3. TITRATION OF CALCIUM CARBONATE WITH VARIOUS ACIDS AND WITH SOIL ACIDOID  
( $\text{CaCO}_3 = 5 \text{ m.e.}$ )

The method of finding the lime requirement of acid soils based on the reaction with  $\text{CaCO}_3$  has been advocated by several workers (1, 5). The fact that the final pH value corresponds to the neutral point would give added weight to the method.

It appeared of interest to determine the titration curve of a soil with  $\text{CaCO}_3$  and also to find out whether a soil, after being partly neutralized with  $\text{Ca(OH)}_2$  or  $\text{NaOH}$ , would take up from  $\text{CaCO}_3$  the remaining portion of Ca to correspond to the equilibrium point. Increasing amounts of  $\text{Ca(OH)}_2$ ,  $\text{Mg(OH)}_2$ , and  $\text{NaOH}$  were added to a soil, and the pH of each mixture was determined after 48 hours' shaking. These suspensions were then shaken with excess of  $\text{CaCO}_3$ ; and the final pH value, as well as the Ca taken up by the soil, was determined in every case. The results are given in table 2.

A close examination of table 2 reveals some interesting facts. It is seen that when the soil acidoids are first neutralized with  $\text{NaOH}$  and then shaken



with  $\text{CaCO}_3$ , the total amount of exchangeable bases, that is, Na plus Ca, remains the same, and the soil is able to take up small amounts of Ca even at pH 9.68. This is possibly due to replacement of a certain amount of Na by Ca. The pH values of the single-base soils were determined before and after  $\text{CaCO}_3$  treatment, and it is worthy of note that though the pH value of the H-soil brought to equilibrium with  $\text{CaCO}_3$  is approximately 7, sodium and calcium soils at higher pH values can still take up some Ca from  $\text{CaCO}_3$ . The total bases at the equilibrium point are higher in the Na-soil than in the Mg-

TABLE 1  
*Exchangeable calcium in H-soils shaken with calcium carbonate*

SOIL NUMBER, M SERIES	1 HOURS' SHAKING		48 HOURS' SHAKING		$\text{NH}_3$ TAKEN UP BY 100 GM. SOIL	T/2 PER 100 GM. SOIL
	pH in equilibrium with $\text{CaCO}_3$	Exchangeable calcium per 100 gm. soil	pH in equilibrium with $\text{CaCO}_3$	Exchangeable calcium per 100 gm. soil		
		m.e.		m.e.	m.e.	m.e.
1	7.12	25.2	6.78	24.4	24.4	23.2
2	7.28	13.2	6.86	16.0	11.6	12.0
3	7.24	15.2	6.79	13.6	13.4	14.6
4	7.29	13.2	6.78	14.4	11.4	12.8
5	7.18	22.8	6.76	21.6	18.6	20.0
6	7.30	10.8	6.90	9.2	9.2	10.0
7	7.25	17.2	6.81	16.8	13.6	28.0
8	7.20	26.8	6.74	25.2	26.2	28.2
9	7.31	8.4	6.99	7.2	8.8	12.4
10	7.20	21.6	6.90	20.0	20.4	16.6
11	7.33	18.0	6.93	14.0	13.0	14.0
12	7.24	19.2	6.88	19.6	19.8	16.24
13	7.37	8.4	6.97	9.2	9.6	9.44
14	7.26	14.8	6.93	15.2	10.6	10.64
16	7.43	7.6	7.00	8.8	6.2	5.84
17	7.32	8.4	6.92	10.4	13.6	10.0
21	7.25	15.2	7.04	14.8	22.6	14.24
22	7.34	9.2	7.01	13.6	12.0	12.32
23	7.28	12.0	6.95	10.0	14.4	12.48

soil or in the Ca-soil. The mutual salt effect of  $\text{CaCO}_3$  and Ca-soil, each suppressing the ionization of the other, is well brought out by these results.

Another noteworthy fact is that exchangeable Ca in a soil containing exchangeable Mg can be determined by the  $\text{K}_2\text{CO}_3$ -acetate-oxalate method of Puri (2). This would seem extraordinary, in view of the fact that Ca and Mg salts are generally precipitated together by oxalates. The reason for this separation in soils lies in the fact that the activity coefficient of a Ca-soil is very much higher than that of a Mg-soil; the latter is therefore extremely insoluble and does not react with potassium oxalate within the time prescribed for this reaction, that is, 15 minutes.

The lime status of a soil (5) is defined as the ratio expressing as percentage

the exchangeable Ca actually present in the soil ( $\text{Ca}_1$ ) over the exchangeable Ca the soil will have when brought into equilibrium with  $\text{CaCO}_3$  ( $\text{Ca}_2$ ), that is,

$$\text{L. S.} = 100 \text{ Ca}_1/\text{Ca}_2$$

It must be pointed out that this ratio can have significance only when exchangeable bases other than Ca are absent, a condition scarcely met with in

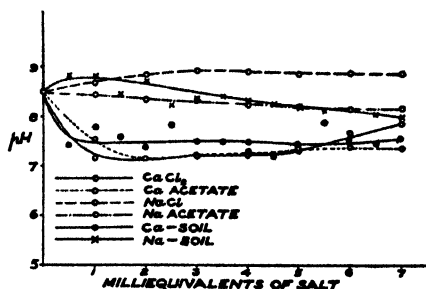


FIG. 4. INFLUENCE OF CALCIUM AND SODIUM SALTS AND OF CORRESPONDING SOILS ON THE pH VALUE OF CALCIUM CARBONATE SUSPENSION

( $\text{CaCO}_3 = 5 \text{ m.e.}$ )

TABLE 2

Exchangeable calcium in H-soil first partly neutralized with  $\text{NaOH}$ ,  $\text{Mg}(\text{OH})_2$ , and  $\text{Ca}(\text{OH})_2$  and then shaken with  $\text{CaCO}_3$

SODIUM HYDROXIDE				MAGNESIUM HYDROXIDE				CALCIUM HYDROXIDE				CALCIUM CARBONATE			
Amount 0.1 N NaOH, in cc.	pH	pH after shaking with $\text{CaCO}_3$	Exchangeable Ca, in cc. 0.1 N per 5 gm. of soil	Amount 0.1 N Mg $(\text{OH})_2$ , in cc.	pH	pH after shaking with $\text{CaCO}_3$	Exchangeable Ca, in cc. 0.1 N per 5 gm. of soil	Amount 0.1 N Ca $(\text{OH})_2$ , in cc.	pH	pH after shaking with $\text{CaCO}_3$	Exchangeable Ca, in cc. 0.1 N per 5 gm. of soil	Amount 0.1 N $\text{CaCO}_3$ , in cc.	pH	pH after shaking with $\text{CaCO}_3$	Exchangeable Ca, in cc. 0.1 N per 5 gm. of soil
0	3.46	7.15	32.2	0	3.46	7.15	32.2	0	3.46	7.15	32.2	0	3.46	7.15	32.2
5	4.53	7.20	30.0	5	3.65	7.09	22.8	5	3.58	7.10	33.6	5	3.67	7.08	28.4
10	4.94	7.34	26.5	10	4.07	7.15	20.8	10	3.86	7.13	33.0	10	3.76	7.08	34.2
20	6.40	7.66	14.6	15	4.63	7.19	17.0	15	4.58	7.18	32.6	20	5.54	7.06	32.8
25	7.68	7.88	8.6	20	6.10	7.30	12.0	20	5.97	7.26	32.2	25	6.75	7.06	34.2
30	9.06	8.54	3.6	25	7.24	7.56	6.8	25	6.94	7.36	33.0	30	7.02	7.04	33.4
35	9.68	9.04	1.2	35	7.80	7.62	3.6	30	7.50	7.33	34.2	35	7.04	7.12	34.4
40	10.20	9.80	0.6	40	7.97	7.68	3.0	35	8.58	8.28	39.4	40	7.07	7.12	31.0
50	10.87	10.34	0.4	50	8.25	7.78	1.6	40	9.14	8.82	40.6	50	7.15	7.08	34.4
..	.....	.....	...	60	8.46	8.03	2.0	50	9.68	9.50	41.4	..	.....	.....	....
..	.....	.....	...	70	8.83	8.12	1.4	..	.....	.....	....	..	.....	.....	....

natural soils. A word of caution, therefore, must be sounded in connection with the interpretation of this constant when different soils are compared. Lime status as a ratio also implies a straight line relationship between the Ca present in the soil and the maximum Ca the soil can take up from  $\text{CaCO}_3$ .

This is correct only within a restricted range of pH, as will be seen from the titration curve of a base-free soil with  $\text{CaCO}_3$  (fig. 5). For practical purposes this range may be quite sufficient, but the inherent defects of this ratio as a fundamental soil constant must be borne in mind if a proper perspective of the true state of affairs is to be maintained.

From the practical point of view, much may be said in favor of the  $\text{CaCO}_3$  equilibrium point as the basis for determining lime requirement of soils. The very slight solubility of  $\text{CaCO}_3$  is a great advantage, because a saturated solution is maintained and the experimental conditions can be easily reproduced, thus leading to a greater uniformity of results in the hands of different workers. It is necessary, however, to exercise judgment in the use of this method. It is evident that even soils requiring no lime might show lime requirement if the method were used indiscriminately without proper regard to the pH value of the soil.

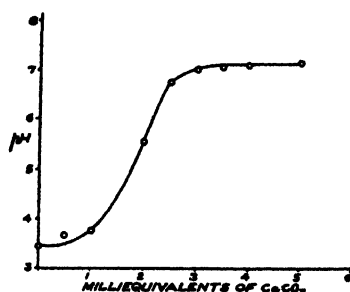


FIG. 5. TITRATION CURVE OF H-SOIL WITH CALCIUM CARBONATE  
(Weight of soil = 5 gm.)

#### SUMMARY

Experimental evidence has been brought forth to show that soil acidoids and single-base soils behave like true acids and salts respectively in their reaction with carbonates of alkali and alkaline earths.

The merits and limitations of the method of finding lime requirement of soils based on the reaction with  $\text{CaCO}_3$  are discussed. The limitations of the ratio known as "lime status" of soils are brought out.

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## ORGANIC PHOSPHATES: I. FIXATION STUDIES WITH THREE DIFFERENT SOIL TYPES<sup>1</sup>

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Spencer and Stewart's (7, 8) investigations on soil penetration of some organic and inorganic phosphates indicate that organic phosphates have promise as phosphatic fertilizers, particularly in places where deep fertilization is desirable. Their studies included percolation experiments in which a 7-inch column of soil with a top-dressing of phosphate was subjected for 3 days to water in amounts equivalent to a 24-inch rainfall.<sup>3</sup> Although several organic phosphates were investigated, only one type of soil, Las Vegas loam (3), occurring in an arid region where alkali is widespread, was used in the work. The organic phosphates employed were derivatives of aliphatic polyhydric alcohols as, for example, glycerol, glucose, and sorbitol, and were used in the form of the calcium salts. Analysis of the water solutions passing through the soil demonstrated that whereas 88–99 per cent of the inorganic phosphate was fixed, only 5–20 per cent of the organic compounds were retained by the soil. These results show that the major portion of the organic phosphate remained in the soluble condition for at least a short time<sup>4</sup> in this particular soil and therefore penetrated it to a greater extent than did the inorganic phosphates.

To examine more critically the potentialities of organic phosphates as fertilizers, it seemed desirable to study their behavior in different soil types and under a variety of soil conditions. Fixation by combination with calcium carbonate and certain iron and aluminum compounds present in soil is not possible for most phosphates of the polyhydric aliphatic compounds so long as they remain in this form, since such salts are soluble in water. A different

<sup>1</sup> In this article the term "phosphate fixation" is used to designate any change to a water-insoluble form. Phosphate in the "insoluble" condition may be considered to be fixed positionally; that is, penetration of the soil to a great depth would not be expected. "Fixed or insoluble phosphate" as used by us does not imply that the phosphate is unavailable for plant growth.

<sup>2</sup> The authors are indebted to K. D. Jacob, W. H. Ross, and L. M. White for facilitating the execution of this work and for the aid received in discussions.

<sup>3</sup> The extent to which organic phosphates will diffuse into the soil under more normal conditions is a quite different matter.

<sup>4</sup> Although the columns of soil were leached with water for 3 days, the major portion of the organic phosphate was probably in the first quarter of the leachings and was therefore in contact with the soil for less than a day. This view is supported by our results listed in table 1.

kind of fixation, involving a reaction with the colloidal matter of the soil, is more likely, but there is no means of determining *a priori* the extent to which this might take place. To obtain some information on this possibility, percolation studies were carried out with Cecil and Norfolk soils which contain widely different amounts of different kinds of colloids. Another important factor that would be expected to influence the fate of organic phosphates is the action of soil microorganisms. The organic phosphates that have so far been suggested as potential fertilizers may be assimilated by bacteria and fungi, since the organic part of these molecules can be utilized as a source of energy. If this is the case, that portion of the phosphate not required for metabolic processes will be liberated and eliminated in the inorganic form and converted to an insoluble state in a high phosphate-fixing soil. Still another path whereby the organic phosphate might be converted to inorganic phosphate is one involving catalytic hydrolysis by phosphatases, enzymes prevalent in living matter. As enzymatic hydrolysis or attack by microorganisms of organic phosphates is relatively slow, very little bacterial action could have taken place under the conditions of Spencer and Stewart's experiments.<sup>5</sup> Time studies were therefore included in our work in order, first, to provide the organisms with an opportunity to attack the organic phosphates and, second, to obtain information on the rate of conversion of soluble to insoluble phosphate. Comparative experiments on sterilized soil were performed with the object of obtaining evidence as to whether or not microorganisms are responsible for the gradual change of soluble to insoluble phosphate. One other factor, the variation in the pH of the soil solution, which might possibly influence the fixation of organic phosphate was also investigated. As the different organic phosphates investigated by Spencer and Stewart yielded similar results, only one, glycerophosphate, was employed in this preliminary study.

Early in the work, it was apparent that our results on Cecil and Norfolk soils were very different from those reported by the previous investigators on Las Vegas soil. In order to prove that the difference was due to the character of the soils rather than to the experimental procedures, a study of Las Vegas soil was also undertaken.

## EXPERIMENTAL

### *Materials*

Sodium glycerophosphate from the Eastman Kodak Company was found to be pure enough for our purposes. Colorimetric estimation showed only traces of inorganic phosphate to be present. The analyses were as follows: calculated for  $\text{Na}_2\text{C}_3\text{H}_7\text{PO}_6 \cdot 5\text{H}_2\text{O}$ —P 10.13,  $\text{H}_2\text{O}$  29.42; found—P 10.67,  $\text{H}_2\text{O}$  26.49. Evidently the glycerophosphate was not wholly in the pentahydrate form. The monopotassium phosphate was an analytically pure specimen.

Norfolk sandy loam and Cecil clay loam were collected in South Carolina,

<sup>5</sup> See footnote 3. In such a short contact period bacterial action could have been only slight.

the former in Edgefield County and the latter in Abbeville County. Norfolk soil was taken from the surface to a depth of 14 inches, and Cecil soil, from a depth of 8 to 35 inches. Las Vegas (3) loam was obtained<sup>6</sup> from Clark County, Nevada. According to information supplied by Spencer, the soil used in his work and in ours came from virtually the same location.<sup>7</sup> The soil was taken from the A horizon. Norfolk soil contained 6.3 per cent clay, 4.2 per cent colloid (included in clay), and 8.5 per cent silt; Cecil soil, 47.2 per cent clay, 41.3 per cent colloid (included in clay), and 16.2 per cent silt; and Las Vegas soil, 1.4 per cent fine gravel, 2.8 per cent coarse sand, 2.5 per cent medium sand, 40.8 per cent fine sand, 25.3 per cent very fine sand, 14.8 per cent silt, 11.6 per cent clay, and 0.4 per cent organic matter; pH of Las Vegas soil, 8.4.<sup>8</sup> Studies on the chemical composition of the colloid in Cecil soil and in Norfolk soil have been reported respectively by Byers, Alexander, and Holmes (2) and by Holmes, Hearn, and Byers (5). The fractions of air-dried Norfolk soil and Cecil soil passing through a 1.90-mm. sieve, and the fraction of Las Vegas soil passing through a 1.27-mm. sieve were used in this work. Specimens of the air-dried Norfolk, Las Vegas, and Cecil soils, when heated at 110° to constant weight, lost 0.1, 0.9, and 2.3 per cent of their weights respectively.

#### *Analytical procedure*

Phosphorus determinations were made in duplicate either colorimetrically or titrimetrically. Results obtained by colorimetric estimation checked with those obtained by titrimetric estimation (1, p. 19-21). In the organic phosphate experiments, the latter method included a preliminary magnesium nitrate fusion. Fiske and Subbarow's (4) micromethod for the estimation of phosphorus was used in colorimetric determinations. Before analysis, the soil extracts were digested with perchloric acid according to the directions of King (6). Not only was the organic phosphate converted to inorganic phosphate, but also the soil extracts from Las Vegas and Norfolk soils, usually yellowish brown, were decolorized, allowing accurate comparison with the standard solution. Sterilization of Las Vegas soil intensified the color of the soil extracts considerably, but no analytical difficulties were encountered. Perchloric acid digestion of Las Vegas soil extracts always resulted in the deposition of some silica. Cecil soil extracts were colorless, and digestion with perchloric acid was not necessary in the inorganic phosphate experiments.

#### *Procedure for carrying out fixation experiments*

The experimental method used in this investigation was a modification of that described by Spencer and Stewart. In order to accommodate the time

<sup>6</sup> Through the courtesy of C. E. Kellogg, of the Soil Survey Division.

<sup>7</sup> From its location on the alkali map (3) the soil would be expected to possess from 0.4-0.5 per cent alkali salts.

<sup>8</sup> This information was supplied by H. G. Byers, of the Soil Chemistry and Physics Research Division.

experiments, the column of soil was wet with the phosphate solution and kept in the moist condition for the required length of time before being washed thoroughly with water to remove soluble phosphate. The operation of leaching either Norfolk or Las Vegas soil was very smooth. Cecil soil, because of its high colloid content, could not be leached very effectively, and it was necessary to employ a washing and decantation process to remove the soluble phosphate.

*Norfolk soil.*—After preliminary trials, the following procedure was employed for most of the experimental work recorded for Norfolk soil. Four hundred grams of air-dried soil was placed in a filtering tube, 1½ inches in diameter and 16 inches in length from the fritted glass filter plate to the top of the tube. The column of soil, about 6 or 7 inches high, was treated with 50 cc. of an aqueous solution containing 0.755 gm. sodium glycerophosphate (equivalent to 0.08 gm. phosphorus), which was the concentration used by Spencer and Stewart. Additional water was added in order to wet the column of soil completely. Both ends of the tube were then stoppered. In a few

TABLE 1  
*Distribution of phosphorus in soil leachings from Norfolk soil*

ORDER OF WASHING	pH	P mgm.	PER CENT OF ADDED P
1	6.6	44.6	55.8
2	7.2	6.1	7.6
3	7.3	2.6	3.3
4	7.3	1.6	2.0
5	7.2	1.2	1.5

experiments, the solid phosphate was added to the surface of the soil, as was done in Spencer and Stewart's work, and the column was moistened with water. Comparative experiments demonstrated that this minor variation in procedure did not affect appreciably the results. Theoretically, however, one would expect a slow reaction to be favored by the addition of phosphate in solution since it will be more evenly distributed throughout the column of soil, and under more carefully controlled long-time experiments significant differences may reveal themselves. The moist soils were allowed to stand at room temperature for various lengths of time, generally 2 to 4 hours, 3, 6, 12, or 24 days, and then each was leached with five 100-cc. portions of water. Representative results of phosphate and pH determinations obtained from the successive fractions draining from Norfolk soil in a 3-day experiment are given in table 1. Inspection of the table shows that by far the greater portion of the phosphate extracted by 500 cc. of water is present in the first 100-cc. portion. The time required to wash the soil varied from 3 to 6 hours. Usually, the longer the moist soil had stood, the slower was the filtration. The combined cloudy leachings were made up to 500 cc., centrifuged, and, if necessary, clarified by

filtration through a thin layer of celite.<sup>9</sup> An aliquot of this solution was subjected to analysis as soon as convenient. If the determination could not be performed immediately, the solution was kept in an ice chest until ready for use. The results obtained in the time studies using sodium glycerophosphate and Norfolk soil are shown in curve I, figure 1. The data were reproducible when the temperature at which the percolation tube stood was constant. Carrying out experiments at temperatures 5° apart, however, influenced the results significantly.

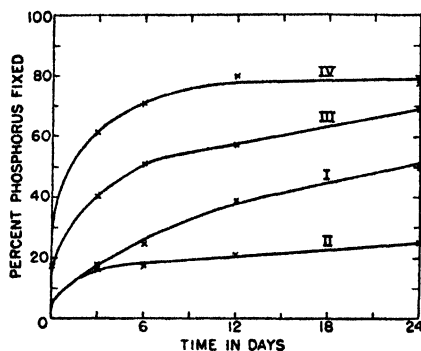


FIG. 1

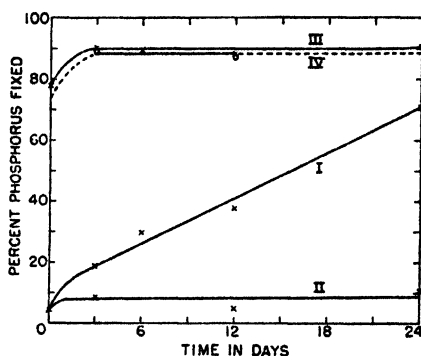


FIG. 2

FIG. 1. TIME DEPENDENCE CURVES OF IMMOBILIZATION OF ORGANIC AND INORGANIC PHOSPHATES BY RAW AND STERILIZED NORFOLK SOIL

*Curve I.* Sodium glycerophosphate in raw soil.

*Curve II.* Sodium glycerophosphate in sterilized soil.

*Curve III.* Monopotassium phosphate in raw soil.

*Curve IV.* Monopotassium phosphate in sterilized soil.

FIG. 2. TIME DEPENDENCE CURVES OF IMMOBILIZATION OF ORGANIC AND INORGANIC PHOSPHATES BY RAW AND STERILIZED LAS VEGAS SOIL

*Curve I.* Sodium glycerophosphate in raw soil.

*Curve II.* Sodium glycerophosphate in sterilized soil.

*Curve III.* Monopotassium phosphate in raw soil.

*Curve IV.* Monopotassium phosphate in sterilized soil.

The comparative study with monopotassium phosphate was carried out in a similar manner. A solution of 0.351 gm. of phosphate (equivalent to 0.08 gm. phosphorus) in water was employed to wet the soil. The leaching operations in these experiments required less time, being completed within 3 hours. The data obtained on the Norfolk soil are compiled in curve III, figure 1.

Phosphate fixation by Norfolk soil, where the pH of the soil solution was varied, was studied by employing the foregoing procedure with the following change. Before the phosphate solution containing either inorganic or organic phosphate was added to the soil, the pH of the solution was adjusted to 5, 6,

<sup>9</sup> Control experiments in which leachings were clarified without celite gave virtually the same results as experiments involving the use of celite.



or 7 by addition of hydrochloric acid. The pH was determined electrometrically. One series of treated soils was allowed to stand for 3 days and another for 6 days before the soluble phosphate was collected. From the results shown in table 2 it is apparent that the variation of the pH of the organic phosphate solutions added to the soil had only a minor effect on the degree of fixation in a 3- or 6-day contact period. Increasing the time of contact, however, would be expected to yield greater differences, inasmuch as the pH affects the activity of phosphatases and microorganisms.

*Las Vegas soil.*—With Las Vegas soil, the experimental investigation was limited to a study of the time dependence of fixation. The procedure described for Norfolk soil was used except that the sodium glycerophosphate solution was adjusted to a pH of 6.0 before addition to the soil. Because of the relatively high alkali salt content of Las Vegas soil, the combined extracts were basic, and the pH ranged from 7.7 to 7.9. The time required to wash the column of soil varied from 5–7 hours. The results obtained in the sodium

TABLE 2  
*Variation in fixation of  $\text{KH}_2\text{PO}_4$  and of sodium glycerophosphate with pH in Norfolk soil*

pH	$\text{KH}_2\text{PO}_4$		SODIUM GLYCEROPHOSPHATE	
	Per cent of P fixed		Per cent of P fixed	
	In 3 days	In 6 days	In 3 days	In 6 days
5	43.6	44.8	21.9	28.6
6	38.9	45.2	24.5	38.6
7	35.6	50.9	21.4	34.2

glycerophosphate and monopotassium phosphate experiments are shown in curves I and III, figure 2.

*Sterilized Norfolk and Las Vegas soils.*—Norfolk and Las Vegas soils were heated at 175°C. for 20 hours. Although some spores may have survived, there can be but little doubt that the major portion of the living matter was destroyed by this treatment. Solutions of sodium glycerophosphate and of monopotassium phosphate were prepared by addition to boiled distilled water. The glassware was sterilized by the usual heat process. Precautions were taken to prevent contamination by bacteria and molds during the various operations. The variation of fixation with time was studied according to the general method already described. Graphs of the results with sodium glycerophosphate and with monopotassium phosphate are presented in figure 1, curves II and IV, and in figure 2, curves II and IV.

*Cecil soil.*—Considerable difficulty was encountered in working with Cecil soil. Water or solutions having a pH of 5 to 7 percolated through a column of soil extremely slowly, whereas more basic solutions did not pass through at all. In the former case, the flow of liquid ceased after 25 to 50 cc. of filtrate had been collected. Addition of water as a fine spray to dampen the soil

and swell the colloid before placement in the tube, and application of either suction or 40 pounds pressure per square inch enhanced percolation moderately. Even under these conditions, however, the procedure was not practical, and reliance was not placed in the phosphate values obtained in the relatively small amount of filtrate. The fact that only traces of phosphate were found was later shown to be significant.

A more reliable, although laborious, procedure was developed for determining the fixation of phosphates by this type of soil. Samples of 100 gm. of the Cecil soil were placed in 250-cc. centrifuge bottles and wet with the phosphate solutions. The solution of sodium glycerophosphate consisted of 0.189 gm. of the phosphate, 20 cc. of water, and sufficient hydrochloric acid to adjust the pH to 6.0. The solution of monopotassium phosphate was prepared by dissolving 0.088 gm. of the phosphate in 20 cc. of water. After the soil was treated with the phosphate solution, additional water, usually 15 cc., was supplied to

TABLE 3  
*Fixation of organic and inorganic phosphate by Cecil soil*

PHOSPHATE	CONDITION OF CECIL SOIL	TIME	P IN EXTRACT	PER CENT OF P FIXED
		days	mgm.	
Sodium glycerophosphate.....	Raw	3	0.93	95.3
	Raw	12	0.08	99.6
	Sterilized	3	2.16	89.2
	Sterilized	12	0.08	99.6
KH <sub>2</sub> PO <sub>4</sub> .....	Raw	3	0.40	98.0
	Raw	12	trace	99.9
	Sterilized	3	0.50	97.5
	Sterilized	12	trace	99.9

moisten the soil completely. After the soils had stood for either 3 or 12 days, 90 cc. of water was added, the mixture was thoroughly shaken for about 30 minutes, when a homogeneous mass was secured, and centrifuged. The supernatant liquid was removed and filtered. This process was repeated three more times. Phosphorus determinations were made on the combined aqueous fractions, the pH of which varied from 6.6-7.0. Typical results obtained in studies on raw and on heat-sterilized Cecil soil are shown in table 3.

#### RESULTS AND DISCUSSION

Our investigation demonstrates that the fixation of glycerophosphate by soils varies markedly from soil type to soil type. Only a minor amount of the organic phosphate as compared to 90 per cent of the inorganic phosphate was fixed by Las Vegas soil when the time of contact between the phosphate and the soil was 3 days or less (fig. 2). These results essentially confirm those of Spencer and Stewart on this type of soil. In the same length of time, 18 per

cent of organic phosphate and only 40 per cent of inorganic phosphate were fixed by Norfolk soil<sup>10</sup> (fig. 1). Under similar conditions, Cecil soil removed virtually all the organic and inorganic phosphate from the soil solution. The trend in the fixation of phosphate by the last two soils follows their colloid content, Norfolk soil containing 4.2 per cent and Cecil soil about 41.3 per cent. The data indicate that these three different soils are particularly well adapted for the study of organic phosphates, since they provide examples of the extreme as well as intermediate degrees of phosphate fixation.

The fixation of organic phosphate by Las Vegas or Norfolk soil was markedly augmented as the contact period was increased. In figure 2, fixation of organic phosphate (curve I) and fixation of inorganic phosphate (curve III) by Las Vegas soil are plotted against time. From an inspection of curve III, it is apparent that the major portion of the inorganic phosphate, in fact 78 per cent in 2 to 4 hours, was removed very rapidly, and that after a few days, no further increase in fixation took place. In contrast to the rapid fixation of inorganic phosphate only 4 per cent of the organic phosphate<sup>11</sup> was fixed in 2 to 4 hours. From this point on, the amount fixed increased continuously and almost linearly with time. After 24 days more than 70 per cent of the original organic phosphate had been converted to an insoluble form. The data from the time studies on Norfolk soil (fig. 1, curves I and III) show that fixation of inorganic phosphate (curve I) was more gradual and much slower than that in Las Vegas soil. In the early stages a smaller quantity of organic phosphate as compared to inorganic phosphate was fixed by Norfolk soil. It is interesting, however, that, after the sixth day, the rate of organic phosphate fixation was virtually the same as the rate of fixation of inorganic phosphate. Cecil soil fixed organic and inorganic phosphate so rapidly and completely that elaborate time studies were not necessary; 95-98 per cent of the inorganic or organic phosphate was fixed in 3 days, and only traces of phosphate remained in solution after 12 days (table 3).

Evidence, favoring the view that the increase in fixation of organic phosphate with time is in large part due to the action of microorganisms on organic phosphate with the liberation and subsequent fixation of the inorganic phosphate,

<sup>10</sup> It is to be pointed out that the A horizon of Norfolk sandy loam, the B horizon of Cecil clay loam, and the A horizon of Las Vegas loam were used in this work. Throughout this article, these soils have been named, for the sake of brevity, *Norfolk soil*, *Cecil soil*, and *Las Vegas soil*, respectively. When these terms are used in making comparisons we do not wish to infer we are comparing, for example, the relative fixation capacities of *Norfolk sandy loam* and *Cecil clay loam*. Instead we are interested in knowing at this stage of the investigation what the behavior of organic phosphate is in two different types of soil (Cecil soil and Norfolk soil) which, because they possess different quantities and kinds of colloidal matter, fix inorganic phosphate in different degrees.

<sup>11</sup> The term "organic phosphate fixation" is used rather loosely in this article, since the phosphate fixed may be in the inorganic form and have resulted from the degradation of the organic phosphate in solution.

was obtained in the studies with heat-sterilized soil. Besides destroying living matter and enzymes, heat sterilization has some effect on the physical and chemical characteristics of the inorganic soil constituents. Parallel experiments conducted with inorganic phosphate indicated the extent of the effect heat had on the fixation capacity of the soils. Curves IV, figures 1 and 2, show that the fixation capacity of Las Vegas soil was scarcely affected, whereas the fixation capacity of Norfolk soil was appreciably increased. Quite different results were obtained with organic phosphate. Fixation was much less in sterilized soil than in raw soil. This was particularly true for Las Vegas soil, where, except for a rapid initial fixation amounting to a few per cent, virtually no increase with time took place. After 24 days only 10 per cent of the phosphate had been fixed as compared to 70 per cent by the raw soil. In sterilized Norfolk soil, the amount of organic phosphate fixed increased very slowly from about 16 per cent in 3 days to about 25 per cent in 24 days. In this case, fixation at 24 days was half that occurring in raw soil for the same period of time. The rapidity with which organic phosphate was removed under normal conditions from solution by Cecil soil would seem to exclude bacterial action and suggests instead its direct combination with the colloidal matter in the soil. As was anticipated, sterilization of this soil did not change appreciably its capacity to fix either organic or inorganic phosphate. From these results as a whole, it is apparent that the action of microorganisms is an important factor in determining the fate of organic phosphates in some soils.

Although only three different types of soil have so far been investigated, it is evident from the results that the composition of the soil is an important factor in determining the extent of fixation of orthophosphates of the polyhydric aliphatic alcohols. Soil high in a certain type of colloidal matter will fix organic phosphates almost as completely as inorganic phosphate. Since this is a rapid process it is doubtful whether glycerophosphate will penetrate such soil to a greater degree than will inorganic phosphates. Soils containing much smaller amounts and a different type of colloidal matter, as Norfolk soil in which immobilization of organic phosphate increases slowly with time, will be penetrated more easily. The soluble organic phosphate, however, will be transformed to inorganic phosphate by the action of microorganisms and, therefore, will be diverted ultimately to the same fate as inorganic phosphate. Calcareous soils, such as Las Vegas soil, will rapidly convert inorganic phosphates to an insoluble condition but will not immediately affect the major portion of the organic phosphate. In this case also the phosphate will gradually be attacked by microorganisms, and as the inorganic phosphate is liberated, it will be immobilized. Although a superficial examination of our results suggests that organic phosphates would have no greater value than inorganic phosphates as phosphatic fertilizers, we do not wish to draw this conclusion at present, since other lines of investigation, still open, may yield more promising results. For example, organic orthophosphates of a different

general type from those thus far studied or certain organic metaphosphates may possibly be stable in soil over long periods of time and may not be fixed by some inorganic phosphate fixing soils.

#### SUMMARY

Comparative experiments were carried out on the immobilization of organic and inorganic phosphate by three different types of soil; namely, Cecil soil, Norfolk soil, and Las Vegas soil.

The fixation of glycerophosphate varied widely with the nature of the soil. In Cecil soil, which possessed about 40 per cent colloidal matter, the organic phosphate was converted almost as rapidly and completely to an insoluble form as was inorganic phosphate.

In Norfolk and Las Vegas soils, the percentage of organic phosphate immobilized increased as the time of contact of the organic phosphate with the soil increased.

Very little increase in fixation of organic phosphate by sterilized Norfolk and Las Vegas soils took place in a contact time of 3 to 24 days, thus supporting the view that the increase in fixation in raw soil is in the main a secondary reaction following the primary action of soil microorganisms on the organic phosphate.

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## BOOK REVIEWS

*Principles and Practice of Bacteriology.* By ARTHUR H. BRYAN AND CHARLES BRYAN. Barnes & Noble, Inc., New York, 1938. Pp. 267, figs. 101. Price: cloth \$2.25, paper \$1.25.

The field of applied bacteriology is constantly expanding. Because of that, there is need for clear-cut guidance, not alone for the student, but also for the worker in control laboratories. The authors of the present work have had this in mind. According to their own statement:

*Principles and Practice of Bacteriology* presents a concise, concrete, and practical reference guide and test for students and workers in both the theory and practice of bacteriology. While no originality is claimed for its content, the unique plan of organization should be of inestimable value to users of the book.

Because bacteriology is basically a laboratory subject, many useful techniques, devices, and practical procedures have been included for both beginning students and practicing bacteriologists.

Quick reference tables and charts, being especially helpful in bacteriology, have been added to the routine subject matter wherever important information may be needed at a glance. The tables include the pathogenic hyphomycetes and yeasts, primary determinative culture media, plant diseases, soil micro-biology, dairy bacteria, veterinary pathogens, human pathogens, dental bacteria, colon typhoid differentiation, and tables of toxins and anti-toxins.

The body of the text is made up of three parts; namely, Introduction, Human Pathogenic Bacteriology, and Serology and Immunology. There are altogether 28 chapters, the titles of which are: History of Bacteriology; General Characteristics of Bacteria; Preparation and Inoculation of Culture Media; Physiological and Chemical Characters as Determinative Procedures; Methods of Destruction of Bacteria; Practical Methods of Examination of Bacteria; Yeasts, Molds, and Actinomycetes including Pathogens; Chromogens; Agricultural and Industrial Microbiology; Dairy, Air, Dust, and Water Bacteriology; Veterinary Bacteriology; Introduction to Pathogenic Bacteriology; The Pyogenic Cocci; The Specific Cocci; The Diphtheria Group; The Tuberculosis or Mycobacteria Group; The Pasteurella Group; Hemophilus Group; The Colon-Typhoid Dysentery Group; The Anaerobic Spore Bearers; Vibrio Group; The Spirochetes; Filters and Filtrable Virus Diseases; Pathogenic Protozoa; Infection and Immunity; Some Useful Serological and Diagnostic Test Methods; Toxin and Antitoxin Tables; and Animal Inoculation, Autogenous and Stock Vaccines. There are 8 appendixes and an index.

Both the teacher and the laboratory worker will welcome this book as a desirable addition to available teaching material.

*Soils and Soil Management.* By CHARLES ERNEST MILLAR. Webb Book Publishing Co., St. Paul, Minn., 1937. Pp. 477, figs. 248, tables 35.

There is a tendency at the present time to stress the management factor of soil study. This may be accounted for in part by local regional and national programs relating to land use. It may also be accounted for by the wide interest in soil conservation including the control of soil erosion.

The author was well aware of this fact when he was writing his book. As he himself notes:

In preparing this text the author has attempted to analyze each soil problem as it might arise on the farm, in the garden, or about the city or country home, before beginning a discussion of ways of solving the problem. It is felt that this practice in analyzing each situation as it presents itself has an educational value beyond the specific information acquired. In addition the author has found it an interesting method of presenting subject matter to his classes.

The volume contains 26 chapters, which the author has named: Selecting a Farm; Observe Soil Formation; Classifying Soils; Fitting the Seed Bed; Maintaining Good Tilth; Cultivating the Crop; Controlling Soil Moisture; Rotating Crops; Making Commercial Fertilizer; Fitting the Fertilizer to the Soil; Fitting the Fertilizer to the Crop; Buying Fertilizers; Applying Fertilizer; Keeping the Soil from Washing; Controlling Soil Blowing; Supplying the Soil with Organic Matter; Building up Soil with Manure; Increasing Profits with Lime; Farming Acid Soils; The Alkali Problem; Adding Nitrogen to the Soil; Studying Soil Life; Managing Sandy Soils; Improving the Pasture; Gardening; and The Home Grounds. There are also a list of laboratory equipment, a glossary, and an index.

It is evident that the author has made an earnest effort to provide helpful information to the landowner. He has indicated effective methods of approach in dealing with the soil problems in different regions and has supplied the reader with references to publications that will readily supplement the information recorded in this book.

*Farm Economics.* By FRANK APP AND ALLEN G. WALLER. J. B. Lippincott Co., New York, 1938. Pp. 700, figs. 248.

The present volume is based on an earlier book on farm economics, by Frank App. It has the merit of dealing with farm economics, management, and distribution in a progressive way. None the less, the authors have evidently had in mind the preparation of their material in such fashion as to be particularly serviceable to producers in the northeastern region of the United States. They are well aware of the rapid changes that have taken place in the organization of both production and marketing. In their own words:

Agriculture in America is recognized as a business. The conduct of this business is of concern not only to those directly engaged in it, but also to the rest of the nation. The invention and use of modern machinery, the building of great cities and the settlement of

our fertile lands make continual changes necessary in the economics of our agricultural production and distribution. The progress of the nation to a large measure depends upon the ability of a portion of the people to produce the food and clothing material necessary for themselves and families and to have left sufficient for several other families. This releases a portion of the population for other pursuits and in turn allows for the progress of civilization.

They also note:

In recent years a vast amount of data have been accumulated which can be used as a measure in gauging farm enterprises. The individual engaged in agriculture must understand not only the physical and biological factors necessary for sound farm enterprise, but also how to apply his farm practice so as to obtain the greatest returns from a farm enterprise. The student may need to consider the ability of the operator to handle such a business. However, the authors have not attempted to measure efficiency in terms of the human operator, but rather in terms of economies and management.

The book contains 19 chapters and an appendix. The topics dealt with are as follows: Farm Life; Size of Farm Business; Production; Farm Balance; Farm Capital and Credit; Types of Farming and Farm Enterprises; Selection of Crops; Selection of Livestock; Farm Layout and Arrangement; Acquiring a Farm; Land Rental; Farm Accounts; Cost Accounts; Cost of Producing Farm Products; Prices of Farm Products; Marketing of Farm Products; Fundamental Principles of Coöperation in Agriculture; Farm Power and Equipment; and Farm Labor.

The authors have undoubtedly rendered a service to the teacher as well as to the progressive farmer. There is a wealth of information in the book. The chapters are followed by lists of questions that should encourage thoughtful inquiry among the readers. The reference material is ample for helping the student to expand his knowledge.

*Landslides and Related Phenomena.* By C. F. STEWART SHARPE. Columbia University Press, New York, 1938. Pp. xii + 137, plates 9, figs. 16. Price \$3.00.

This book is particularly timely in view of the nation-wide organization of soil conservation programs. The student of soils is aware of the fact that there is a type of erosion which has been designated as *geological* erosion. It involves mass movements of soil and rock and is the broader phase of the movement of surface material to lower levels. Both water and air currents are major factors in determining the character of the transportation of soil material.

The author of the present volume has tried to dramatize his subject and has done it successfully. In the words of Douglas Johnson, who wrote the foreword:

Imagine a landmass upon which no rain falls, no rivers flow, no glaciers form, no waves beat, no winds blow. Let chemical and mechanical disintegration disrupt the rocks, and gravity exert its downward pull. On such a landmass earth and rock will move ceaselessly



from higher to lower levels, slopes will soften, relief will fade. Given time enough, the whole will be reduced to a featureless plane of disintegrated rock debris.

A study of the mass-movement of rock and rock debris on such a land would be full of interest for the geomorphologist. How much more interesting is the study on such an earth as ours, where water and ice in varying quantities give endless variety to the processes and forms involved. It is to these processes and their resulting forms that Dr. Sharpe turns his attention in the pages which follow.

To the above may be added the statement of the author himself. He says:

The importance of landslides and other types of mass-movement in the denudation of the lands has long been underestimated. Some of these movements progress so slowly that their presence is scarcely realized. Others, sudden or catastrophic in nature, are overlooked because our uniformitarian concept of geology stresses the continuous action of four agencies; running water, winds, waves, and moving ice. Landslides and related phenomena are not isolated processes but are part of a continuous series grading from dry detritus movement into fluvial and glacial transportation. Any adequate classification of landslide phenomena must include related movements of flow type and must show the relation of the entire group to fluvial and glacial purposes.

The body of the book is made up of a foreword by Douglas Johnson, a preface by the author, and 7 chapters followed by a selected bibliography and an index. The titles of the several chapters are: Significance of Mass-Movement; Types of Mass-Movement; Slow Flowage; Rapid Flowage; Landslide; Subsidence; and Conclusion.

The author has dealt with his subject ably. He has developed some new points of view and has established certain conceptions which will provide a most helpful guide to students of surface geology and of land use.

*Plant Biochemistry*. Revised Edition. By WILLIAM EDWARD TOTTINGHAM. Burgess Publishing Co., Minneapolis, Minn., 1937. Pp. 249, figs. 98, tables 104. Price \$4.25.

The biochemistry of plants has been made the subject of some of the newer research projects. Interest in biochemistry is traceable to studies of plant nutrition. Water and sand culture methods are being employed in many laboratories. In fact, the term *hydroponics* was invented to describe the growing of plants in artificial culture media. Aside from plant nutrition, there is the question of animal and human nutrition. There is also the question relating to the use of plant products in the manufacture of various industrial commodities. Here we find the term *chemurgy* used frequently. Altogether, therefore, plant biochemistry may be considered a rapidly expanding field for the investigator, the teacher, and the industrialist.

The author is well aware of the accumulation of new data and information. He says in his preface:

The rapid development of the subject has necessitated rather extensive annual revision of the notes from which this text has evolved. This indicates to be sure, that relatively frequent revision of text books in the field will be necessary for some time. Fortunately, this task

stands likely to be much lightened by the annual reviews of biochemistry which have developed. Citations of the literature have been introduced freely, partly as evidence to support positions taken by the author and partly to induce breadth of reading on the part of the student. Much care has been exercised in consulting the original articles for accuracy as to both citation and reference. An opportunity to revise the original edition has been used for amplifying and modernizing discussional features.

The book contains 10 chapters and an appendix. For the convenience of the reader, the titles used to designate the several chapters are herewith given. They are: General Aspects; The Photosynthesis; the Metabolism of Carbohydrates; Fat Metabolism; The Metabolism of Nitrogen Compounds; Physico-Chemical Relations of the Plant Cell; the Nature and Function of Enzymes; Chemical Aspects of Respiration; Salt Nutrition; and Climatic Effects in Metabolism. The materials of metabolism are discussed in the appendix.

It will be noted that considerable attention has been given to the general subject of metabolism, including that related to carbohydrates, fats, and nitrogen compounds. The nature and functions of the plant cells, the nature and functions of enzymes and of mineral salts, and, likewise, the influence of climatic environment on metabolism have been reviewed by the author. The more important references are also given.

From the instructor's point of view, *Plant Biochemistry* should prove decidedly helpful.

✓ *The Chemistry of Plant Constituents.* By OLE GISVOLD AND CHARLES H. ROGERS. Burgess Publishing Co., Minneapolis, Minn., 1938. Pp. 309, tables 28. Price \$3.50.

The number of compounds found in plants is without end. This will account for the specialized approach that is adopted by many compilers of data on the chemistry of plant constituents. Gisvold and Rogers' conception of their task is indicated as follows:

The subject matter of this book treats of the chemistry of plant constituents and some of the theories advanced to explain their formations. Various probable and also possible reactions that may be involved in the formation of the many known and characteristic parts of large molecules found in plants have been presented and discussed. The very fact that, starting with first or simple materials, a plant is able to synthesize complex molecules through the agencies necessary to its development would indicate that a myriad of complicated reactions take place. To postulate a theory for the formation of an alkaloid of complex composition from one of the first products of photosynthesis, formaldehyde, might appear at first to be beyond the scope of the most vivid imagination. Nevertheless, many syntheses like this one are actually accomplished by plants and, perhaps, by the presentation of many theories, a few may offer to science explanations of transitions which at times have seemed to be enigmatical. Also, attention is directed to certain organic reactions that may either be involved in the formation of plant constituents or aid in characterizing and proving the structures of these products of plant life.

The treatise contains 15 chapters and a bibliography. The chapters are named, respectively: Introduction; Carbohydrates; Vegetable Fats; Plant

and Insect Waxes; Phytosterols; Proteins; Alkaloids; Glycosides; The Anthocyanins and Anthoxanthins; Carotinoids; Tannins; Terpenes and Oxygenated Terpenes; Vitamins; Enzymes; and Products of Fermentation.

It will be noted that major consideration is given to carbohydrates, fats, waxes, phytosterols, plant substances containing nitrogen, and a number of products qualitatively important even though quantitatively they might represent a minor portion of the plant tissues. The authors summarize some of the present-day knowledge of fermentation products including alcohols and organic acids.

The student, the teacher, and the investigator will find this work a convenient source of ably compiled and interpreted data.

*The Foundations of Nutrition.* Third Edition. By MARY SWARTZ ROSE. The Macmillan Company, New York, 1938. Pp. xi + 625, frontispiece, figs. 116, tables 9. Price \$3.50.

This is a revision of the first and second editions, published in 1927 and 1933, respectively. The extent of the revision that was necessary is described by the author. She says:

In preparing this third edition it has been gratifying to note that in the main the researches of the past five years have only served to establish more firmly the foundations of nutrition as originally outlined in 1927. At the same time, it has been necessary to make a thorough revision of every topic because there have been many additions to our knowledge of every dietary essential. These new advances enable us to understand human requirements better and to use our common food materials to increasingly good advantage. In 1933 only three of the vitamins had been crystallized and in case of only two had any clear picture of chemical structure begun to emerge. In this edition it is possible to state not only that six have been crystallized and chemically identified, but also that three of them have been prepared artificially. The use of highly concentrated preparations or of pure crystals has helped to advance rapidly our understanding of the functions of the vitamins and great activity in the assay of foods for vitamin values has furnished a mass of data, necessitating complete revision of all tables and dietaries.

The present volume contains 26 chapters, 9 appendixes, and an index. The titles of the several chapters, which follow, will acquaint the reader with the author's approach to the subject. They are: Historical Introduction; The Body's Need for Energy and Food as the Source of Supply; The Energy Requirement of Adults; Factors Causing Variation in the Basal Metabolism of Individuals; The Energy Requirement of Children; Shortage and Surplus of Calories; Protein as Body Building Material; Mineral Elements and Water as Body Building Material; Mineral Elements and Water as Regulators of Body Processes; Vitamin A as a Regulator of Body Processes; Vitamin B ( $B_1$ ) as a Regulator of Body Processes; Vitamin C as a Regulator of Body Processes; Vitamin D as a Regulator of Body Processes; Vitamin G as a Regulator of Body Processes; Vitamins of Undetermined Significance in Human Nutrition; Contributions to the Diet Made by Various Types of Food Materials; Milk; The Foods Derived from Grains; Vegetables and Fruits; Eggs,

Cheese, Nuts, Meat and Other Flesh Foods; Fat, Sugars and Other Sweets; The Construction of an Adequate Diet: Diets for Adults; Food Needs of Pre-School and Kindergarten Children; Food Needs of Elementary and High School Boys and Girls; Well Balanced Diets for Family Groups; and Special Food Needs of Mothers and Babies.

*The Foundations of Nutrition* may well be accepted as a valuable contribution to the field of preventive medicine. The proper nutrition of animals and of humans plays an important rôle in maintaining good health. The author has rendered a service to teachers in schools and colleges, and, beyond that, to the large group of extension workers and lecturers who are expected to keep the public acquainted with rational procedures in the purchase, the handling, and the cooking of foods as well as in the preparation of suitable dietaries.

*Le Sistemazioni Idraulico-Agrarie.* By ALBERTO OLIVA. S. A. G. Barbera, Firenze, Italy, 1938. Pp. 356, figs. 102.

This book is devoted to the consideration of soil erosion as it applies particularly to the soils of Italy. Many centuries of soil exploitation, soil conservation, and soil building have left a deep impression on soil management practices in that country. The traveler in Italy is early impressed by the painstaking, and often exhaustive, labor devoted to the protecting of the land against gully and sheet erosion. He will be impressed no less by the land drainage practices, by terracing, forestation, and grassland farming as a part of the soil conservation and soil erosion control movement. From that point of view, European countries have traveled much farther along the road of soil saving than have the newer countries of the two Americas. Despite all effort to the contrary, there is still a serious soil erosion problem in Italy. This is indicated by the following statement of the author:

Soil erosion has assumed serious proportions in Italy owing to the prevalent hilly and mountainous character of the territory, to the extension of Miocene and Pliocene clays and Eocene sand, also to the violent rainfall with frequent cloud-bursts.

Since very early times the requirements of Italian agriculture have necessitated the taking of measures against erosion. This explains the evolution in Italy of a special technique by means of which the more serious effects of the erosion have been successfully checked or at least mitigated.

During the last half century the technique of the measures for prevention of soil erosion made further progress in the direction of conservation and utilisation of some part of the rain water for the benefit of the crops during the periods of drought, that is to say, by establishing what the author calls "water economy." Surprising results have been achieved by this technique, especially on the Tuscan hillsides between Florence, Pisa and Siena.

The protection of the soil against rain-water and the utilization for the benefit of crops is called hydraulic and agricultural regulation or simple "regulation."

We may also note from the author's statement:

Many hitherto unknown aspects of Italian agricultural progress, and the secrets of some of the most interesting Italian landscapes are revealed in this volume. In fact the Italian soil regulation works, more than the natural forms of the land, create the orderly and artistic tone of the Italian country.

The body of the book consists of an introduction, 7 chapters, and summaries in English and German. There are also a bibliography, nomenclature, and 3 indexes. The several chapters are entitled, respectively: Concetto e limiti delle sistemazioni; De correlazioni generali delle sistemazioni e di loro particolari aspetti nei terreni di pianura; Le sistemazioni di pianura; Le sistemazioni collinari intensive o bonifiche collinari; Le sistemazioni estensive collinari e di bassa e media montagna; Direttive sulle sistemazioni del suolo declive e forme anomale; and Elementi dei costi delle sistemazioni.

Students of soils and economics will find much of interest in this book. There are also more or less direct relations to the sociological aspect of rural life.

*Soil Science Society of America. Vol. II. Proceedings 1937.* The Soil Science Society of America, F. B. Smith, Sec.-Treas., Gainesville, Fla., 1938. Pp. ix + 602. Price \$5.00.

The Soil Science Society of America is the American Section of the International Society of Soil Science. It is also an affiliate of the American Society of Agronomy.

The present volume is more than a mere collection of the papers presented at the 1937 annual meeting of the society. The Proceedings record the officers of the society, the section officers, and the names of the sections themselves. They are Soil Physics, Soil Chemistry, Soil Microbiology, Soil Fertility, Soil Morphology, and Soil Technology. Under the headings of these sections are reported a total of 102 papers. There is also a record of the business meetings, committee reports, and announcements.

Despite the limited funds for publication, the officers of the society have done very creditable work in publishing the material presented at the 1937 annual meeting. These Proceedings are, unquestionably, a distinct addition in the field of soil science, particularly as it is being developed by American workers.

JACOB G. LIPMAN

# OBSERVATIONS REGARDING SOILS OF NORTHERN AND CENTRAL MEXICO

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In connection with selenium investigations conducted by this Bureau, a field trip<sup>2</sup> was recently made through northern and central Mexico. During the trip the soils<sup>3</sup> occurring in the region were studied as opportunity offered, and certain profile samples were collected for laboratory examination. The profiles described should not be taken as representing carefully defined soil series. Geographical names were assigned them only for the purpose of identification.

The itinerary (fig. 1) was from El Paso through Chihuahua, Torreon, Saltillo, and Monterrey; thence southward to Mexico City, and from Mexico City northwest through Queretaro to Irapuato. The return trip was via the Mexico City-Laredo Highway.

Observations were made of soils developed under widely varied conditions. These include differences in elevation from near sea-level to the summit of Navado de Toluca (approximately 15,000 feet); annual average rainfall ranging from 100 mm. (3.9 inches) to 3,000 mm. (118.1 inches); temperatures ranging from mild temperature to subtropical, and vegetation from scant shrub and grass to coniferous, deciduous, or dense, almost tropical, forests. The agricultural conditions were equally diverse. These include dry farming with a wide variety of crops, ranching, and farming where irrigation has been practiced for centuries as well as in more recently developed areas. Soils were observed which are erosive on gentle slopes; whereas other soils showed little or no evidence of erosion on long and exceedingly steep cultivated slopes.

Tropical soils, which exist in the southern part of Mexico, were not included in the itinerary.

## METHODS

The soil samples were treated according to the analytical practices of this laboratory. The mechanical analyses were made by the pipette method

<sup>1</sup> The writers wish to express their appreciation for the helpful suggestions and criticisms given by Horace G. Byers during the preparation of this paper.

<sup>2</sup> The Mexican government was represented by José Figueroa, whose knowledge of local conditions and whose energetic assistance were extremely valuable.

<sup>3</sup> The soils have been grouped in accordance with the principles outlined by Marbut (13), Kellogg (11), and Shaw (20).

described by Olmstead, Alexander, and Middleton (15). The approximate amount of organic matter determined by the hydrogen peroxide method is included with the mechanical analyses. All the chemical analyses except those for selenium and organic matter were made according to the procedure described by Robinson (16). The organic matter was determined by the combustion method as detailed by Alexander and Byers (1). Selenium was determined by the method outlined by Robinson, et al. (17) and by Williams (22).

The colloids were extracted three to eight times from 100 to 1,000 gm. of soil with the aid of a supercentrifuge operating at 1,650 revolutions per minute, as described by Brown and Byers (3). It is presumed that very few of the colloid particles exceed  $0.3 \mu$  in diameter and most of them are much less.

The pH values of the air-dried soils were determined by the hydrogen electrode as described by Bailey (2), and were checked by the glass electrode. The approximate salt content was determined by the electrolytic bridge as described by Davis (9).

Certain derived data were calculated from the analytical results and are included in the tables. The discussions of these data and of the analytical results follow the field descriptions of the soils.

#### RESULTS OF THE INVESTIGATION

##### *Gray desert soils*

The first part of the trip southward from El Paso to Chihuahua was along a section of the old Camino Real—a road built from Mexico City to Santa Fe by Spanish viceroys before the days of Mexican independence. This is through a region of gray and red desert soils in which the dominant surface soil colors range from light gray to red. These soils are developed in a broad belt extending from El Paso southeastward to Torreon and Parras in Coahuila. Field observations indicate that the boundary of this group coincided roughly with the 200-mm. rainfall, as shown in figure 1. Isolated areas were observed, however, somewhat beyond this limit. Average monthly temperatures in this region range from about 41 to 77°F. (10). Rainfall is distributed throughout the year but is heavier during the summer months.

The desert soils are developed in a region characterized by a series of northwest-southeast mountain ranges and broad intervening structural valleys. Elevations within the valleys range from 3,500 to 4,500 feet (and those of the higher peaks from 7,000 to 8,000 feet). The mountains, which have precipitous slopes, consist of interbedded sandstones, shales, and limestones. In places these formations are capped or intruded by materials of igneous origin. Adjacent to the mountains are extensive areas of alluvial fans consisting largely of stone and coarse gravel. For greater distances the material is finer textured, largely silt, and is of lake-laid or of eolian origin. In many of the broader valleys the lowest elevations are temporary or permanent lakes. These are known locally as lagunas.



FIG. 1. RAINFALL MAP OF A PART OF MEXICO, SHOWING THE LOCATIONS OF THE PROFILES EXAMINED

The locations of analyzed samples are marked by solid black circles; those of other samples examined, by six-pointed stars. The isohyetal lines show the rainfall in millimeters; transpositions are made in the text.



Vegetation within the valleys is of the desert shrub type. It consists mainly of mesquite (*Prosopis* sp.), huisache (*Vachellia farnesiana*), catclaw (*Minosa* sp.), yucca (*Yucca* sp.), and cactus (*Opuntia* sp.). In places there is a sparse covering of short grasses, chiefly grama (*Bouteloua* sp.). Coarse grasses, mainly burro (*Scleropogon brevifolius*) and alkali scaton (*Sporobolus airoides*), are found in the laguna basins. The mountain slopes are sparsely covered with small oak (*Quercus* sp.) and other shrubs.

Regional characteristics are well expressed in the soils developed from old alluvial lake-laid or eolian-deposited materials found in the broad valleys. These materials are finer textured and, generally speaking, have remained in place for a longer period than the coarse gravelly materials of the alluvial fans. Because of their finer texture they are more responsive to soil-forming processes. Characteristics common to these soils are: scattering of highly polished pebbles, commonly referred to as the desert pavement; slightly cemented layer varying in thickness from one-eighth to one-half inch and broken into polygons, sometimes called desert crust; light gray layer of finely granular structure extending to depths of  $1\frac{1}{2}$  to 6 inches; a slightly heavier horizon with cloddy structure. Although soils in which the regional characteristics are well developed may be observed at various points from El Paso southward, 41 miles north of Torreon a profile was noted which best revealed these characteristics. A description of the profile follows:

*Torreon sandy clay loam*

1. 0- $1\frac{1}{2}$  inches, light gray sandy clay, with the upper one-half inch slightly cemented. The remainder of this layer has finely granular structure. This layer does not effervesce with dilute hydrochloric acid.
2.  $1\frac{1}{2}$ -12 inches, gray to light grayish brown somewhat heavier sandy clay, with medium to coarse cloddy structure; noncalcareous.
3. 12-20 inches, light grayish brown clay loam with slightly prismatic structure. This layer is calcareous. It contains numerous grass roots.
4. 20-32 inches, light gray silty clay loam with soft crumb structure. It is likewise calcareous, but is distinctly gray and contains fewer grass roots than the layer above.
5. 32-60 inches, light gray silt loam with small limestone fragments. It has pulverulent structure, is calcareous, and contains some charcoal fragments. The origin of the charcoal in this layer is problematical. It is probably the remains of a brush root which has burned deeply into the ground.

The profile is situated on nearly level topography. It is developed under sparse shrub vegetation and an average annual rainfall of 8 inches.<sup>4</sup>

Observations made at a number of locations on comparable topography indicate a close correlation between the depth and the texture of the surface layer. In clay or clay loam textures this layer varies from 1 to  $1\frac{1}{2}$  inches in depth; whereas in silt loams the variation is generally from  $1\frac{1}{2}$  to 6 inches. In

<sup>4</sup> A 40-year average as recorded by a private station at Tlahualilo at approximately the same elevation 8 miles north of the profile.

every instance, where the material was not cemented, finely granular structure was evident in this layer.

Soils developed from the old alluvial fans vary both in surface texture and in degree of profile development in contrast to the rather uniform development on the finer valley materials. In general, the texture varies from coarse sandy loam to gritty clay loam. Depths to the underlying gravel in the sandy soils vary from 6 inches to 3 feet; whereas in the clay loams the range is 3 or more feet. In the coarse sandy loams there is scant differentiation into horizons. In the clay loams the differentiation is similar to that of the valley soils, but the dominating colors are reddish brown to red in contrast to the gray soils developed from the more silty materials.

The Torreon sandy clay loam is nearly a typical gray desert soil. It is characteristic of an enormous area. Associated with it are azonal soils. The laboratory data of this profile are given in tables 1 to 4.

The mechanical analyses are shown in table 1. Although slight morphological differences in the soil were observed between the 12-20-inch and the 20-32-inch depths, these together constitute the zone of carbonate accumulation. The greatest accumulation of colloid occurs in the third layer, which is probably the mean high level water penetration. The increase in silt content with depth suggests that the parent material was lake land or of eolian origin.

The chemical analyses (table 2) of the soil give additional supplementary information about the development of this profile. The low calcium content and the absence of carbonates indicate complete removal of calcium carbonate from the first 12 inches of the soil and an accumulation in layers 3 and 4, the mean maximum depth of rain water penetration corresponding to the lower depth. The high potassium and sodium indicate incomplete decomposition of feldspars. The feldspars and the low degree of leaching of the soil are together responsible for the pH values found in layers 1 and 2.

The organic matter of horizon 5, as calculated from carbon present, is 2.12 per cent. Microscopic inspection of the soil disclosed many black particles, more or less decomposed. It is apparent that charcoal particles are present in considerable amount. Hence the use of the Wolff factor in this case is misleading.

The chemical analyses of the colloids are shown in table 3. The high organic matter in the colloid of horizon 5 also confirms the presence of carbon as shown in the soil. The presence of much more sodium in the colloid of horizon 1 than in horizons 2 and 3, in spite of thorough washing during colloid extraction, explains in part the high pH of this horizon. The high silica content throughout the profile indicates relatively little hydrolysis of the clay minerals whether translocated or not.

The derived data in table 4 more specifically indicate the slight variability in composition of the clay minerals. The colloids of the third layer show slightly lower ratios of silica to iron oxide, to the bases, and to water of con-

TABLE 1  
*Mechanical analyses\* of Mexican soils*

SAMPLE NUMBER	HORI- SON	DEPTH	FINE GRAVEL, 2-1 MM.	COURSE SAND, 1-0.5 MM.	MEDIUM SAND, 0.5-0.25 MM.	FINE SAND, 0.25-0.1 MM.	VERY FINE SAND 0.1-0.05 MM.	SILT, 0.05- 0.005 MM.	CLAY, 0.005- 0 MM.	COL- LOID, 0.002- 0 MM.	ORGANIC MATTER BY H <sub>2</sub> O <sub>2</sub>
		inches	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Torreón sandy clay loam, Torreón, Coahuila</i>											
B-20799	1	0-1½	0.0	0.4	2.2	27.7	22.6	19.0	27.5	19.3	0.3
B-20800	2	1½-12	0.0	0.2	1.5	22.1	21.0	21.0	33.9	25.8	0.1
B-20801	3	12-20	0.2	0.4	2.1	20.0	18.2	20.4	38.1	28.2	0.2
B-20802	4	20-32	1.4	1.8	1.3	13.7	20.8	27.5	33.2	22.1	0.2
B-20803	5	32-60	0.3	0.4	0.4	9.5	15.6	44.5	28.9	22.6	0.1
<i>Juarez clay, Juárez, Chihuahua</i>											
B-20717	1	0-6	1.4	1.9	1.3	4.15	14.5	13.2	52.7	42.9	0.2
B-20718	2	6-12	0.7	0.9	0.7	7.9	12.2	14.9	61.2	49.4	0.2
B-20719	3	12-27	0.4	0.6	0.7	8.2	11.2	18.0	58.9	48.7	0.0
B-20720	4	27-36	0.9	1.2	0.9	7.1	9.5	15.7	62.7	52.2	0.4
B-20721	5	36-48	0.6	1.6	1.0	8.2	10.1	13.0	63.6	55.0	0.4
<i>Agua Nueva sandy loam, Agua Nueva, Chihuahua</i>											
B-20733	1	0-4	10.3	15.5	12.3	30.4	12.3	5.0	12.6	10.0	1.1
B-20734	2	4-10	12.6	18.2	12.0	27.1	10.5	6.1	12.3	11.1	0.9
B-20735	3	10-18	7.6	14.3	11.3	28.6	13.0	6.9	16.4	14.2	1.5
B-20736	4	18-30	3.1	7.5	9.8	38.7	16.6	5.4	18.2	16.5	0.1
B-20737	5	30-42	0.2	5.8	8.2	26.5	10.5	7.6	38.7	31.7	0.1
B-20738	6	42+	1.3	4.1	7.3	27.2	12.3	12.4	34.6	24.2	0.0
<i>Irapuato clay loam, Irapuato, Guanajuato</i>											
B-20896	1	0-10	0.5	1.0	0.9	8.2	13.0	41.6	30.8	24.8	3.3
B-20897	2	10-23	0.2	0.5	0.6	7.2	18.0	47.5	25.5	21.1	0.3
B-20898	3	23-28	0.1	0.1	0.2	8.6	40.0	34.2	16.4	13.2	0.0
B-20899	4	28-35	0.0	0.1	0.6	3.5	9.1	41.0	45.2	37.4	0.1
B-20900	5	35-55	0.1	0.1	0.1	0.7	2.7	26.4	69.4	63.7	0.3
B-20901	6	55-97	0.8	0.9	0.6	1.6	2.8	22.1	70.6	59.6	0.3
B-20902	7	97-144	0.7	0.9	0.7	3.0	8.6	34.1	51.1	40.9	0.7
B-20903	8	144+	0.3	1.1	1.0	2.8	7.6	24.9	61.3	48.2	0.8
<i>Queretaro clay, Queretaro, Queretaro</i>											
B-20947	1	0-3	1.1	1.2	0.8	2.5	2.7	21.7	67.9	57.5	1.7
B-20948	2	3-8	0.8	0.7	0.8	2.4	3.3	20.3	69.8	60.5	1.7
B-20949	3	8-30	0.1	0.3	0.5	1.7	2.0	15.5	78.6	69.4	1.2
B-20950	4	30-48	0.1	0.2	0.2	1.1	1.8	12.7	82.5	73.0	1.2
<i>Tamasunchale clay, Tamasunchale, San Luis Potosí</i>											
B-20973	1	0-3	0.3	0.7	0.7	2.2	2.4	21.3	66.3	58.4	5.2
B-20974	2	3-20	0.0	0.2	0.3	0.8	0.9	8.7	87.0	84.1	1.9
B-20975	3	20-48	0.0	0.1	0.1	0.4	0.4	3.6	94.5	92.3	0.7
B-20976	4	48+	38.5	23.8	7.7	9.8	4.9	7.3	7.7	3.1	0.1

\* Analyses by T. M. Shaw and E. F. Miles.

stitution than do the colloids of the layer immediately above or below. The ratios of iron oxide to alumina and of water to alumina are higher, and the ratios of water to iron oxide is lower, in the colloids of the third horizon than in the colloids of the eluviated layers or of the layer nearer the parent material. It seems apparent that although the conditions throughout the profile are nearly alike, the portion of the colloid in the upper layers suffering the greatest hydrolysis is that most readily translocated.

In many respects the colloid of this soil resembles that of Phillips sandy loam from Montana described by Brown, Rice, and Byers (5), although the latter is developed under somewhat higher rainfall and at a lower temperature than the former. The parent materials of the two soils are very similar in composition.

### *Intrazonal soils*

Of the intrazonal soils the solonchak soils are closely associated with the gray desert soils. They are found in many of the laguna basins which are subject to periodic flooding and subsequent evaporation, and likewise where the water table is near the surface and where, consequently, there is considerable capillary movement of water upwards. These soils vary in texture from silt loam to clay, and in color from light to dark gray or black. They have typically developed "buffalo wallow" microrelief; finely granular structure in the surface soil; and in places at lower depths, especially in the heavier textures, well-developed prismatic structure. An excellent example is found near Meoqui, Chihuahua. Here the surface soil is a heavy, black clay highly impregnated with light colored salts. The vegetation is chiefly coarse grass. In a nearby field further salinization has resulted through irrigation without adequate drainage. No profile sample of this soil was taken.

The solonchak soils are more widespread than the solonetz in northern Mexico. The reasons are obvious if the low rainfall of the area is considered. In most places, however, the rainfall is sufficient to have moistened the soil enough to produce hydrolysis of the primary rock minerals, but it has not been adequate to permit removal of these salts by percolating water. The flow of ground water is slow, if it occurs at all, and is at such depth as to have given no material aid in removing the soluble salts from the soil. In particularly favorable conditions near the laguna basins, however, enough surface water has penetrated the soil after each torrential rain to have caused a partial removal of soluble salts, and the usual solonchak profile in many places has some of the properties of a solonetz.

Most of the solonchak soils noted have light gray, highly dispersed surface horizons underlain at depths of 4 to 6 inches by heavier silt loam with slightly granular structure. This is underlain at depths of 20 to 30 inches by silt or loamy fine sand. The vegetation is usually coarse grasses such as burro grass and alkali scaton. An extensive area of solonchak soil lies 60 to 70 miles south of Juarez; and another, in the laguna basin northwest of El Sauz, Chihuahua.

TABLE 2  
Chemical analyses\* of Mexican soils

SAMPLE NUMBER	HORIZON	DEPTH	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	IGNITION LOSS	TOTAL	OR-GANIC MATTER†	CO <sub>2</sub>	N	SOLUBLE SALTS	pH	Se
		inches	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	p.p.m.		p.p.m.
<i>Torreón sandy clay loam, Torreón, Coahuila</i>																					
B-20799	1	0-1½	70.38	2.90	14.60	1.08	1.50	3.82	1.79	0.42	0.07	0.10	0.08	3.39	100.13	0.71	0.00	0.05	360	8.1	....
B-20800	2	1½-12	69.89	3.18	15.10	1.27	1.50	3.76	1.82	0.42	0.11	0.08	0.05	3.38	100.53	0.52	0.00	0.04	780	7.9	....
B-20801	3	12-20	66.36	2.89	14.43	1.17	4.27	3.54	1.58	0.39	0.10	0.09	0.10	5.54	100.46	0.35	2.42	0.04	1,630	7.9	....
B-20802	4	20-32	66.68	2.66	13.49	0.90	5.10	3.16	2.20	0.40	0.09	0.04	0.11	5.63	100.46	0.19	2.86	0.02	880	8.0	....
B-20803	5	32-60	67.38	2.76	13.75	0.95	3.62	3.28	1.80	0.40	0.08	0.05	0.01	5.95	100.03	2.12	1.89	0.02	660	8.2	....
<i>Juárez clay, Juárez, Chihuahua</i>																					
B-20717	1	0-6	57.77	3.96	13.58	2.22	8.33	2.76	2.10	0.52	0.11	0.18	0.09	8.82	100.44	0.90	5.24	0.05	3,250	8.8	....
B-20718	2	6-12	55.56	4.28	13.46	2.42	8.80	2.62	2.28	0.51	0.12	0.21	0.18	9.74	100.18	0.89	5.74	0.04	7,960	8.6	....
B-20719	3	12-27	52.45	4.24	13.18	2.85	10.60	2.57	2.14	0.52	0.11	0.23	0.73	10.90	100.25	0.77	6.92	0.03	12,600	8.1	....
B-20720	4	27-36	44.12	3.90	11.57	3.02	16.36	2.10	1.87	0.44	0.09	0.25	0.51	15.65	99.88	0.79	11.59	0.03	14,500	8.3	....
B-20721	5	36-48	48.11	4.45	12.76	3.24	12.62	2.28	2.32	0.58	0.09	0.22	0.41	13.00	100.03	0.62	9.09	0.04	13,320	8.5	....
<i>Agua Nueva sandy loam, Agua Nueva, Chihuahua</i>																					
B-20733	1	0-4	77.00	2.93	9.75	0.61	1.17	3.55	1.78	0.33	0.06	0.12	0.04	2.28	99.62	1.42	0.37	0.07	420	8.1	....
B-20734	2	4-10	76.20	2.78	9.77	0.57	1.47	3.77	1.82	0.28	0.04	0.07	0.02	3.04	99.83	1.08	0.61	0.06	450	7.9	....
B-20735	3	10-18	75.00	2.74	9.98	0.60	2.27	3.72	1.79	0.23	0.05	0.05	0.01	3.29	99.73	0.77	1.15	0.04	470	8.1	....
B-20736	4	18-30	73.30	2.89	9.88	0.72	3.36	3.58	2.06	0.23	0.04	0.06	0.03	3.84	100.08	0.39	1.93	0.03	640	8.2	....
B-20737	5	30-42	57.40	3.23	8.91	1.67	12.90	2.65	1.71	0.24	0.09	0.04	0.03	11.00	99.87	0.34	8.62	0.02	3,240	9.3	....
B-20738	6	42+	55.30	2.85	8.80	1.18	14.64	2.50	1.82	0.25	0.07	0.03	0.03	12.52	99.99	0.13	10.59	0.01	4,770	9.7	....

*Irapuato clay loam, Irapuato, Guanajuato*

	1	0-10	63.21	4.72	14.61	1.91	2.29	2.04	2.07	0.69	0.13	0.15	0.12	8.59	100.53	5.05	0.00	0.28	960	7.6	1.5
B-20896	2	10-23	65.60	5.07	14.87	2.08	2.65	1.91	1.92	0.81	0.13	0.10	0.07	5.02	100.23	1.47	0.57	0.09	1,230	8.1	0.03
B-20897	3	23-28	66.69	5.05	15.21	2.11	2.34	1.95	2.46	0.73	0.12	0.06	0.11	3.48	100.31	0.69	0.18	0.03	2,730	8.0	0.05
B-20898	4	28-35	66.08	5.00	15.98	1.80	1.82	1.50	2.08	0.74	0.11	0.06	0.08	5.29	100.54	1.09	0.00	0.04	2,730	7.8	0.05
B-20899	5	35-55	60.99	6.14	18.09	2.22	1.75	1.79	1.28	0.71	0.14	0.09	0.07	7.21	100.48	1.50	0.20	0.06	1,470	8.0	0.03
B-20900	6	55-97	63.43	5.07	16.97	1.86	1.82	1.70	1.11	0.66	0.12	0.07	0.08	7.19	100.08	1.22	0.76	0.04	840	8.0	0.02
B-20901	7	97-144	68.03	3.63	15.65	1.07	1.47	2.06	1.45	0.47	0.09	0.06	0.06	5.90	99.94	0.13	0.67	0.03	960	8.3	0.01
B-20902	8	144-216	63.31	5.55	17.25	2.12	1.62	2.18	1.48	0.70	0.12	0.12	0.05	5.68	100.18	0.25	0.00	0.02	890	8.2	0.01

*Queretaro clay, Queretaro, Queretaro*

	1	0-3	60.79	4.55	16.94	1.52	2.92	1.30	1.06	0.84	0.11	0.09	0.09	10.34	100.55	4.40	0.00	0.20	690	7.8	....
B-20947	2	3-8	61.38	4.62	17.52	1.47	2.75	1.25	1.04	0.85	0.12	0.09	0.08	9.30	100.47	3.42	0.00	0.14	510	7.9	....
B-20948	3	8-30	61.97	4.88	17.66	1.46	2.33	1.18	0.77	0.85	0.11	0.08	0.06	8.78	100.13	2.19	0.00	0.09	250	7.7	....
B-20949	4	30-48	62.73	4.95	18.16	1.63	2.00	1.09	0.82	0.81	0.11	0.05	0.05	7.98	100.11	1.47	0.00	0.06	200	7.5	....

*Tamazunchale clay, Tamazunchale, San Luis Potosi*

	1	0-3	47.90	8.47	24.06	0.49	1.15	0.08	0.05	1.56	0.16	0.09	0.11	16.31	100.44	8.00	0.00	0.26	670	6.9	....
B-20973	2	3-20	44.24	9.26	31.44	0.37	0.55	0.04	0.06	1.36	0.08	0.06	0.06	12.93	100.45	1.74	0.00	0.08	<149	6.0	....
B-20974	3	20-48	40.35	9.32	34.52	0.40	0.62	0.04	0.09	1.04	0.06	0.03	0.06	13.65	100.18	1.35	0.00	0.05	<149	6.1	....
B-20975	Lime-	48+	0.84	0.09	0.37	0.50	55.31	Tr.	0.08	Tr.	0.03	0.03	0.10	42.90	100.25	....	43.05	....	260	8.5	....

\* Determined by Glen Edgington, except analyses of Agua Nueva profile and the following analyses: organic matter, CO<sub>2</sub>, and N by W. M. Noble; soluble salts by I. C. Brown; pH by E. H. Bailey; and Se by K. T. Williams.

† Determined by the combustion method (CO<sub>2</sub> × 0.471).

‡ CO<sub>2</sub> of the carbonates.

TABLE 3  
Chemical analyses\* of Mexican soil colloids

SAMPLE NUMBER	HORI- ZON	DEPTH	COL- LOID EXTRA- CTED	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	LOST- TION LOSS	TOTAL	OR- GANIC MAT- TER†	CO <sub>2</sub>	N
		inches	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Torreón sandy clay loam Torreón, Coahuila</i>																			
B-20799	1	0-1½	40	55.80	6.94	18.91	2.86	1.74	3.61	0.46	0.56	0.11	0.39	0.06	8.03	99.47	1.50	0.00	0.14
B-20800	2	1½-12	61	56.60	6.28	20.32	2.80	1.49	3.13	0.07	0.48	0.13	0.22	0.02	7.88	99.62	0.85	0.05	0.09
B-20801	3	12-20	45	54.40	7.17	17.13	3.06	4.66	3.06	0.07	0.54	0.19	0.31	0.01	9.64	100.24	0.57	2.27	0.09
B-20802	4	20-32	48	56.15	7.22	18.67	2.71	3.35	2.24	0.35	0.49	0.08	0.13	0.07	8.69	100.15	0.58	1.05	0.09
B-20803	5	32-60	41	51.38	6.06	18.48	2.56	3.04	1.85	0.29	0.46	0.10	0.09	0.06	15.42	99.79	8.46	0.71	0.04
<i>Juárez clay, Juárez, Chihuahua</i>																			
B-20717	1	0-6	84	48.89	7.75	16.26	4.30	6.72	2.39	0.32	0.67	0.12	0.23	0.03	12.44	100.12	1.24	3.84	0.09
B-20718	2	6-12	73	48.70	8.10	15.89	4.39	7.00	2.28	0.35	0.65	0.09	0.29	0.05	12.22	100.01	0.82	3.58	0.09
B-20719	3	12-27	87	48.65	7.65	15.87	4.34	7.33	2.27	0.35	0.55	0.08	0.33	0.07	12.07	99.56	0.83	0.40	0.08
B-20720	4	27-36	79	43.60	6.80	13.47	4.99	12.07	2.06	0.47	0.58	0.07	0.33	0.10	15.05	99.59	0.97	8.33	0.08
B-20721	5	36-48	68	47.50	7.74	14.94	5.31	8.25	2.12	0.36	0.62	0.06	0.33	0.11	12.81	100.15	0.69	5.04	0.06
<i>Agua Nueva sandy loam, Agua Nueva, Chihuahua</i>																			
B-20733	1	0-4	32	53.95	6.79	15.95	3.09	3.26	3.18	0.56	0.51	0.15	0.28	0.18	12.50	100.44	5.32	0.05	0.39
B-20734	2	4-10	40	54.95	6.86	15.38	3.27	4.44	3.08	0.52	0.46	0.14	0.26	0.08	12.37	99.94	4.43	0.74	0.32
B-20735	3	10-18	45	52.60	7.08	15.49	3.44	5.03	2.98	0.43	0.43	0.12	0.20	0.07	11.94	99.81	3.04	1.52	0.22
B-20736	4	18-30	67	54.80	7.37	15.45	3.99	4.53	2.73	0.53	0.44	0.09	0.12	0.00	10.45	100.50	1.46	1.13	0.12
B-20737	5	30-42	83	55.90	7.22	14.33	5.44	4.61	2.80	0.76	0.45	0.15	0.05	0.02	8.81	100.54	0.70	0.42	0.07
B-20738	6	42+	35	55.35	7.54	14.87	4.79	4.67	2.38	0.81	0.51	0.10	0.10	0.02	8.71	99.84	0.33	0.56	0.06

*Irapuato clay loam, Irapuato, Guanajuato*

	1	0-10	62	49.20	9.97	20.92	1.92	1.53	1.56	0.21	0.60	0.13	0.26	0.10	13.86	100.26	4.64	0.00	0.35
B-20896	2	10-23	59	49.40	10.85	21.70	2.25	1.33	1.55	0.18	0.51	0.15	0.16	0.03	12.15	100.26	2.72	0.00	0.19
B-20897	3	23-28	60	48.85	11.09	21.78	2.84	1.32	1.40	0.26	0.58	0.16	0.15	0.02	11.54	99.99	2.14	0.00	0.15
B-20898	4	28-35	70	51.30	9.80	21.76	2.39	1.19	1.26	0.27	0.62	0.08	0.11	0.01	11.02	99.81	1.42	0.00	0.11
B-20899	5	35-55	68	50.80	9.73	22.39	2.52	1.20	1.16	0.20	0.56	0.10	0.10	0.01	11.26	100.03	1.45	0.00	0.10
B-20900	6	55-97	80	52.30	8.21	23.02	2.33	1.20	1.34	0.26	0.56	0.05	0.06	0.02	10.59	99.94	1.42	0.00	0.08
B-20901	7	97-144	54	55.26	7.31	22.59	1.90	1.16	0.99	0.00	0.61	0.06	0.09	0.02	10.15	100.14	0.87	0.00	0.11
B-20902	8	144-216	61	52.80	8.83	21.89	2.79	1.63	1.13	0.00	0.59	0.10	0.22	0.02	10.11	100.09	0.55	0.00	0.07

*Queretaro clay, Queretaro, Queretaro*

	1	0-3	57	53.10	7.00	21.81	2.09	2.11	1.04	0.09	0.64	0.07	0.15	0.05	11.46	99.61	2.37	0.06	0.18
B-20947	2	3-8	64	53.40	7.20	22.39	2.06	1.87	0.93	0.06	0.67	0.06	0.14	0.03	11.38	100.19	2.22	0.06	0.13
B-20948	3	8-30	63	54.15	7.20	22.03	1.95	1.97	0.88	0.07	0.78	0.11	0.09	0.01	10.78	100.02	1.64	0.00	0.08
B-20949	4	30-48	74	54.19	7.46	22.29	1.92	1.74	0.56	0.00	0.90	0.06	0.15	0.02	10.50	99.79	1.23	0.00	0.08

*Tamasunchale clay, Tamasunchale, San Luis Potosi*

	1	0-3	54	37.35	10.65	32.86	0.50	1.01	0.12	0.00	1.15	0.05	0.29	0.04	16.25	100.27	3.68	0.05	0.21
B-20973	2	3-20	82	38.95	10.40	34.64	0.28	0.53	0.12	0.00	0.97	0.19	0.09	0.02	14.01	100.20	1.62	0.05	0.08
B-20974	3	20-48	85	39.50	10.03	34.65	0.28	0.57	0.11	0.00	0.93	0.10	0.09	0.02	13.93	100.21	1.32	0.00	0.08

\* Organic matter, CO<sub>2</sub>, and N determined by W. M. Noble; sample B-20803 determined by Glen Edington.† Determined by the combustion method (CO<sub>2</sub> × 0.471).‡ CO<sub>2</sub> of the carbonates.



TABLE 4  
Derived data: Mexican soil colloids

SAMPLE NUMBER	HORIZON	DEPTH  inches	SiO <sub>2</sub> FeO <sub>2</sub> ·Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub> FeO <sub>2</sub>		SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>		FeO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub> TOTAL BASES*	SiO <sub>2</sub> H <sub>2</sub> O†		H <sub>2</sub> O FeO <sub>2</sub> ·Al <sub>2</sub> O <sub>3</sub>		H <sub>2</sub> O FeO <sub>2</sub>		H <sub>2</sub> O Al <sub>2</sub> O <sub>3</sub>		COMBINED WATER‡ per cent	COMBINED WATER OF THE SOIL ACID§ per cent	
Torreon sandy clay loam, Torreon, Coahuila																						
B-20799	1	0-1½	3.89	21.41	5.01	0.234	6.30	1.82	2.14	11.77	2.75	6.53	9.33									
B-20800	2	1½-12	3.95	23.98	4.72	0.197	7.29	1.82	2.17	13.16	2.59	6.98	9.40									
B-20801	3	12-20	4.26	20.18	5.40	0.268	6.43	1.74	2.45	11.60	3.10	6.80	9.62									
B-20802	4	20-32	4.12	20.79	5.13	0.247	7.10	1.79	2.30	11.61	2.87	7.06	9.61									
B-20803	5	32-60	3.45	19.90	4.17	0.209	6.04	1.60	2.16	12.44	2.61	6.25	9.36									
Juarez clay, Juarez, Chihuahua																						
B-20717	1	0-6	3.90	16.78	5.04	0.300	4.79	1.41	2.77	11.90	3.57	7.36	10.97									
B-20718	2	6-12	3.93	16.02	5.21	0.325	4.45	1.33	2.96	12.05	3.92	7.62	11.46									
B-20719	3	12-27	3.93	17.09	5.11	0.299	4.82	1.48	2.66	11.55	3.46	6.84	10.42									
B-20720	4	27-36	4.16	17.09	5.50	0.322	4.06	1.46	2.85	11.70	3.77	5.75	9.90									
B-20721	5	36-48	4.06	16.41	5.40	0.329	4.11	1.35	3.01	12.16	4.00	7.08	11.20									
Agua Nueva sandy loam, Agua Nueva, Chihuahua																						
B-20733	1	0-4	4.51	21.15	5.78	0.273	4.97	1.56	2.89	13.55	3.70	7.13	10.94									
B-20734	2	4-10	4.71	21.29	6.02	0.283	5.24	1.60	2.94	13.30	3.76	7.20	10.86									
B-20735	3	10-18	4.47	19.73	5.76	0.292	4.91	1.49	3.00	13.24	3.87	7.38	11.10									
B-20736	4	18-30	4.61	19.75	6.02	0.305	4.77	1.45	3.18	13.62	4.15	7.86	11.83									
B-20737	5	30-42	5.02	20.60	6.62	0.321	3.46	1.34	3.75	15.36	4.94	7.69	12.66									
B-20738	6	42+	4.77	19.55	6.32	0.318	4.05	1.40	3.41	13.96	4.52	7.82	12.02									
Irapuato clay loam, Irapuato, Guanajuato																						
B-20896	1	0-10	3.06	13.14	4.00	0.304	8.50	1.35	2.27	9.74	2.96	9.22	11.49									
B-20897	2	10-23	2.93	12.10	3.87	0.299	8.41	1.32	2.22	9.16	2.93	9.43	11.50									
B-20898	3	23-28	2.89	11.75	3.83	0.297	7.22	1.31	2.21	8.95	2.92	9.40	11.68									
B-20899	4	28-35	3.10	13.70	4.01	0.341	8.58	1.35	2.29	10.15	2.97	9.60	11.53									
B-20900	5	35-55	3.02	13.87	3.86	0.278	8.52	1.31	2.31	10.59	2.95	9.81	11.76									
B-20901	6	55-97	3.14	16.95	3.85	0.227	8.92	1.44	2.18	11.76	2.67	9.17	11.20									
B-20902	7	97-144	3.45	20.11	4.16	0.207	11.86	1.55	2.22	12.98	2.68	9.28	11.01									
B-20903	8	144-216	3.38	15.42	4.30	0.279	7.98	1.37	2.47	11.25	3.14	9.56	10.93									
Queretaro clay, Queretaro, Queretaro																						
B-20947	1	0-3	3.43	20.20	4.13	0.204	8.80	1.46	2.35	13.84	2.83	9.03	11.14									
B-20948	2	3-8	3.36	19.75	4.15	0.210	9.46	1.48	2.27	13.85	2.80	9.10	11.05									
B-20949	3	8-30	3.45	20.05	4.18	0.209	9.70	1.46	2.36	13.74	2.86	9.14	11.01									
B-20950	4	30-48	3.40	19.31	4.13	0.214	10.67	1.51	2.25	12.79	2.73	9.27	10.93									
Tamazunchale clay, Tamazunchale, San Luis Potosi																						
B-20973	1	0-3	1.60	9.33	1.93	0.207	20.40	0.751	2.13	12.29	2.57	12.62	13.66									
B-20974	2	3-20	1.60	9.96	1.91	0.192	39.30	0.916	1.75	10.88	2.10	12.44	12.94									
B-20975	3	20-48	1.63	10.44	1.93	0.187	60.55	0.912	1.79	11.45	2.12	12.61	13.12									

\* Oxides of Mg, Ca, K, and Na.

† Water of combination plus the water equivalent of the bases.

‡ Ignition loss less the organic matter.

§ Water of combination plus the water equivalent of the bases, corrected for the organic matter and carbonate content.

The profile collected 62 miles south of Juarez, Chihuahua, on nearly level topography is described as follows:

*Juarez clay*

1. 0-6 inches, grayish brown clay with finely granular structure in the upper 1-inch layer, followed by fine nut structure below. The material is stiff and only moderately plastic under moist conditions. It is low in organic matter.

2. 6-12 inches, grayish brown clay breaking into medium clods ranging from 1 to 1½ inches in diameter.

3. 12-27 inches, brown crumbly clay. This layer contains some carbonates. There is only a gradual transition in texture from the layer above, but there is a sharp transition to a finer texture below, accompanied by a change in color. The structure appears slightly prismatic.

4. 27-36 inches, light reddish brown, crumbly clay with large white spots of carbonates. This is the zone of maximum carbonate accumulation.

5. 36-48+ inches, reddish brown stiff calcareous clay. It contains less moisture than the layer above.

A similar profile was collected near the eastern limits of the same laguna near Agua Neuva, about 50 miles north of Chihuahua. This is developed on low level elevations slightly above the laguna basin and bordering the mountain slopes to the east. The cover is a fair stand of short grasses, chiefly grama. The profile is as follows:

*Agua Neuva sandy loam*

1. 0-4 inches, medium gray sandy loam with powderlike structure in the upper one-half inch and fine granular below.

2. 4-10 inches, dark gray, granular sandy loam high in organic matter. Slightly heavier than above.

3. 10-18 inches, dark gray sandy loam with small white spots of carbonates and with fine granular structure. Crushes to a dark yellowish gray.

4. 18-30 inches, light grayish yellow with penetrations of dark gray along root and worm channels and with numerous white accumulations of carbonates. The material is a sandy loam which crushes readily into fine crumbs.

5. 30-42 inches, pale yellow stiff clay or sandy clay highly impregnated with carbonates.

6. 42+ inches, gray crushing to a pale yellowish gray stiff sandy clay, probably waterlaid. High in carbonates.

The relatively high organic content to a depth of 18 inches distinguishes this profile from the regional profile, which is light gray and low in organic matter. The abundance of worm channels, which are rare in most of the soils of this region, suggests a more uniformly high moisture content. This is probably due to added water drained from the adjoining slopes.

Although these two profiles offer some interesting contrasts, they have certain features in common. On this account they are discussed together.

The mechanical analyses are presented in table 1. The soils are not the same in texture; one is a clay, the other is a sandy loam. The first has an average of 60 per cent clay and of 50 per cent colloid and has approximately equal amounts of silt and of very fine sand. In the second profile the textural

relations are reversed. It is sandy, low in silt, and in all but the lowest two horizons the clay and colloid are also low. There is no evidence of extensive translocation of fine material in either profile. The lowest two horizons of both may have been enriched by eluviation, but it is more probable that this textural division of the profile is inherent in the parent material. It is not impossible that the change in texture may mark a change in the depth of an ancient lake. If so, the lower layers were deposited when the lake was deep, and the upper layers when the shore line was near.

The chemical analyses (table 2) of both soils likewise offer no sure evidence of the manner of deposition of parent material, nor do they suggest any marked translocation of material within either profile. They do show, however, that the upper layers of both soils have been leached, particularly in the Agua Nueva soil. The leaching is shown particularly by the removal of calcium carbonate and soluble salts from the upper layers. The Juarez clay is certainly a solonchak soil. The soluble salts are high: 1.26, 1.45, and 1.33 per cent in horizons 3, 4, and 5. They are chiefly chlorides, sulfates, and carbonates. The Agua Nueva sandy loam has 0.32 and 0.48 per cent of soluble salts in the lowest two horizons, but the layers above are relatively free from soluble salts. Leaching has been more thorough in this profile than in the Juarez clay profile, and the pH of 9.3 and 9.7 of the lowest two layers of the Agua Nueva profile are doubtless caused by sodium carbonate. Comparisons of quantities of sodium in the soils with those in the colloid indicate incomplete hydrolysis of the feldspars (see table 3). The greater amount of organic matter in the Agua Nueva soil indicates that the removal of soluble salts from the surface horizon has made it adaptable to a larger number of plants or a greater growth.

The chemical analyses of the colloids (table 3) likewise indicate no material alteration or translocation of the mineral content except sodium. Sodium is low in both soils. It is usually the first to go if leaching takes place. It may be noted, however, that the sodium of the colloids is highest for those horizons in each soil having the most soluble salts and commonly the higher pH (see table 2).

If any changes in the colloids had taken place in the development of the two saline profiles, it would be shown by a comparison of one constituent with another (table 4). The data in each profile are, in general, uniform. No marked differences in various parts of the profiles are indicated. All of the derived data show this uniformity. Slight differences are doubtless accidental or are caused by differences in the composition of the parent material. Be that as it may, the average ratios of silica to sesquioxides and to alumina of the Juarez colloids are 3.99 and 5.25, and the corresponding ratios of the Agua Nueva colloids are 4.68 and 6.26. And a like comparison of water with the sesquioxides and alumina gives ratios of 2.85 and 3.74 for the first, and 3.20 and 4.15 for the second profile. It seems evident that little if any silica has been lost, as compared to alumina, by the more thorough leaching, at a high pH, of the Agua

Neuva profile. Also, the average combined water of the soil acid of the colloid of the Juarez clay is 10.80 per cent and that of the Agua Neuva sandy loam is 11.57. These data show the effect of salinization and desalinization of the soil colloid. Greater leaching of the Agua Neuva profile would have made these differences even greater.

The utilization of the unirrigated desert soils is confined almost entirely to grazing. In many places the insufficiency of supplies of water for stock precludes the use of cattle, and grazing is limited largely to horses, goats, and sheep; in some areas, such as the Bolson de Mapimi, even horses and goats are not to be found, although apparently pasturage is ample. A few areas bordering Rio Grande and its tributaries; Rio del Carmen near Villa Ahumada, Chihuahua; Rio Chuviscar and Rio San Pedro south of the city of Chihuahua in the same state; and Rio Nazas in the vicinity of Torreon, Coahuila, are irrigated and utilized for the production of cotton, corn, small grains, and truck crops. Ninety per cent of the total cotton production of Mexico comes from these regions.

The irrigated districts are densely populated (12) whereas the remainder of the region is sparsely populated. Most of the irrigated soils are light gray silt or clay loams. They are low in organic matter and have a tendency to clod or puddle easily under irrigation. In the Rio Grande Valley attempts have been made to correct these conditions by the addition of fine sand from the adjoining uplands. Some of the irrigation projects have been under tillage for hundreds of years, whereas others, especially in the vicinity of Delicias, Chihuahua, along Rio San Pedro, have only recently been established.

Miscellaneous land types in the same general area include the sand dunes south of Ciudad Juarez, Chihuahua, and the rough, rocky, mountainous slopes, which are, generally speaking, land without soil.

#### *Chernozem soils*

An extensive area of dark gray to black soils is developed on the region surrounding Villa Juarez, Tamaulipas. No profiles were taken for laboratory analysis from this region, but certain field observations were made.

A second area of dark gray to black soils is found surrounding Irapuato in the state of Guanajuato and the city of Queretaro to the east in Queretaro. The physiography in this region consists of a series of broad east-west valleys bordered by low mountain ranges. The mountains are capped by lava flows which are dominantly basalt. The soils developed on the mountain slopes are shallow, dark gray to black, and high in organic matter. They are underlain by either caliche or basaltic fragmented materials which are coated with calcium carbonate. The valley soils are heavy black clay to a depth of 6 or more feet. A profile observed 12 miles east of Queretaro, Queretaro, is as follows:

#### *Queretaro clay*

1. 0-3 inches, black heavy clay with finely granular structure.
2. 3-8 inches, black heavy clay with granular structure. Breaks into irregular clods.

3. 8-30 inches, black heavy clay, which breaks into large prisms 6 to 8 inches in diameter.
4. 30-48 inches, very dark gray to black, smooth, heavy clay.
5. 48-60 inches, very dark gray to black heavy clay.

The profile is on nearly level topography. The present vegetation is short grass. The original vegetation on both the mountain sides and valleys is said to have been small trees, mainly oak, and brush.

In another profile, on level topography in the valley of the Guanajuato south of Irapuato (pl. 1, fig. 1), the upper 28 inches consist of overwash materials, below which dark heavy clay extends to a depth of 97 inches. At this point it is underlain by light gray stiff clay. A description of the profile follows:

*Irapuato clay loam*

1. 0-10 inches, black heavy clay loam crushing to coarse granules. It has numerous perforations, many of which are made by plant roots.
2. 10-23 inches, dark grayish brown silty clay with white carbonate spots. The structure is distinctly laminated above but prismatic below. This layer is penetrated by grass roots.
3. 23-28 inches, brown very fine sandy loam.
4. 28-35 inches, very dark gray clay loam breaking naturally into 4- to 6-inch prisms.
5. 35-55 inches, black heavy clay forming columns similar to those above; calcareous.
6. 55-97 inches, black heavy clay breaking into large cubical clods; calcareous.
7. 97-144 inches, light gray, stiff, calcareous clay with massive structure.
8. 144+ inches, dark red plastic clay.

The soils of this region contrast with certain chernozem profiles observed near Villa Juarez. The dark colored valley soils are at an elevation of approximately 6,000 feet; whereas the soils in the vicinity of Villa Juarez are at elevations of 2,500 feet or less. The former are developed under a rainfall of 400 (15.75 inches) to 800 mm. (31.5 inches); and the latter, under much higher rainfall. The average temperature in the Irapuato region ranges from 59 to 68°F. compared to 77° near Villa Juarez. Although the profiles examined in the Irapuato region are highly calcareous, no definite zone of lime accumulation comparable to that observed in the profile south of Villa Juarez was observed. The dark colored material in the profiles near Irapuato was observed to depths of more than 6 feet; in the vicinity of Villa Juarez the maximum depth of the dark material is approximately 30 inches.

The origin of the dark colored valley soils in the Irapuato region is an interesting question. Inasmuch as parts of these valleys are flooded at intervals of 3 to 5 years, it is possible that the unusual thickness of the dark colored soil is due to the slow accumulation of materials high in calcium carbonate and organic matter from the surrounding mountain sides by slope wash. It is more probable, however, that the soils have literally "swallowed themselves." Partly because of the heavy textures, these soils shrink so much during the long dry periods that wide, deep cracks are formed. Finely granular surface materials are washed or fall into the cracks. This mechanical process operating over a long period would give rise to soils with rather deep, dark solums.

Field observations indicate that the valley soils are low in alkalis. On

drying, the heavy clay surface soil flocculates into coarse granules. This greatly facilitates tillage operations.

Small grains, corn, tomatoes, peppers, and other vegetables are raised on a commercial scale on the dark colored valley soils. Because of the insufficiency of rainfall, most of these crops are raised under irrigation.

The chernozem profile from Irapuato and the profile from Queretaro in many respects closely resemble each other. Certain differences, however, will be noted in the joint discussion of the analytical data (tables 1, 2, 3, 4) of the two soils.

The mechanical analyses (table 1) show the differences in textural character of the two soils. The Queretaro clay profile is very high in clay as well as colloid. The first three horizons of the profile of Irapuato clay loam contain only about one-third as much clay and colloid as do the first two horizons of the profile from Queretaro. But horizons 5 and 6 of the Irapuato profile average a little lower in colloid and clay, and are higher in silt content than the more directly comparable horizons 2, 3, and 4 of the Queretaro soil. In both profiles the two fine sand fractions are low except in the first three horizons of the Irapuato soil. The explanation is simple. The Irapuato soil has been repeatedly flooded by Guanajuato River, which carries large quantities of silt from the slimes of the mines at Guanajuato, which have been operated for more than 200 years. A part of the suspended material in this flood water, added to the natural slope wash, has built up the soil to a depth of 28 or more inches, and a part has probably been carried deeper, as the percolating water penetrates to greater depths of the profile. It seems certain that the first 28 inches are not wholly derived from the same parent material as the soil below (7) although the selenium content indicates that not more than the first 10 inches have been deposited since the operation of the mines began.

The chemical analyses (table 2) likewise show that about 28 inches of the material have been deposited on the original parent material of the Irapuato clay loam. The averages of the silica, magnesium, calcium, and sodium are somewhat higher in the upper part than in the older and deeper part, and the averages of the iron oxide and alumina are lower. The percentage of organic matter decreases from 5.05 in horizon 1 to 0.69 in horizon 3; increases to 1.09 and 1.50 in the next two horizons; and decreases below. Two zones of carbonate accumulation in corresponding parts of the old and new divisions of the profile also occur. The soluble salts, however, have penetrated deeper than 28 inches. They are high in horizons 2, 3, 4, and 5, but are highest in horizons 3 and 4. The soluble salts do not appear to have materially affected the pH of the layers where they are high. In fact, the pH of the top of the buried soil (horizon 4) is 7.8, and the soluble salts are as high as in horizon 3 where the pH is 8.0. The surface layer has a pH of 7.6, but the soluble salts are lower than in horizon 2 where the pH is 8.1. Presumably the material added to the soil is being formed into a new profile, much like the old, in spite of the disturbing effect of the comparatively recent additions.

In many respects the Queretaro profile (table 2) is like the old and the new parts of the Irapuato profile. It is, on the whole, less alkaline, more thoroughly leached of carbonates, and consequently it contains less soluble salts in all its parts. The somewhat higher percentages of calcium, potassium, and sodium in the first two layers, as compared to horizons 3 and 4, are probably not the result of flooding. These constituents are apparently returned to the upper layers by plants much more rapidly than percolating water could remove them, and a part is certainly still combined in the partially decayed plant residues that have so thoroughly blackened the upper layers of the soil.

The distribution of selenium in the Irapuato soil is largely confined to the first horizon. Its presence in larger amount in this layer suggests that it is furnished chiefly by the additions from the mine slimes (7).

The analyses of the colloids (table 3), except in a few details, are uniform throughout each profile. The colloids of the more recently added first three horizons of the Irapuato soil are, for the most part, somewhat lower in silica and alumina and higher in iron, calcium, potassium, sodium, manganese, phosphorus, sulfur, and organic matter than are those of the deeper and older horizons. The colloids in each part do not differ greatly, as is usual in chernozem profiles (5). Likewise, the colloids of the Queretaro soil do not show marked variation. The similarity of the two chernozem soils is close.

The derived data in table 4 present additional evidence of the conditions just mentioned. The ratios of the various constituents, one or more to another, as well as the combined water and the combined water of the soil acid show the same uniformity mentioned. One of the unusual differences in the Irapuato colloids is the lower ratios of silica to iron oxide and of water to iron oxide in the first three horizons as compared with the deeper horizons. The flood waters have doubtless added this iron to the soil colloid. This is the only evidence that the derived data present of the difference in origin of the two parts of the Irapuato soil.

#### *Lateritic soils*

The lateritic soils have certain characteristics strikingly in contrast with those of the chernozems. Red is the dominant color. This contrasts with the dark gray to black colors which prevail in the chernozems. The soil has a high content of organic matter, a pH ranging from neutral to slightly acid, and a smooth texture. This contrasts with the granular surface horizons, low in organic matter, and the highly calcareous, less leached subsoils of the chernozems. These lateritic soils are highly resistant to erosion, whereas the chernozems frequently show evidences of erosion on gentle slopes.

A few miles north of Tamazunchale the surface configuration changes from a relatively smooth plain to deeply dissected topography. Southward from Tamazunchale there is a rapid ascent through mountainous topography for approximately 75 miles. The change in elevation ranges from approximately 5,000 feet at Tamazunchale to 7,300 feet 10 miles beyond Jacala. The pre-

precipitation throughout most of this distance ranges from 2,000 mm. (78.74 inches) to 3,000 mm. (118.11 inches) per annum, and average temperatures range from 68 to 77°F. This is a region of lateritic soils, but certain variations occur.

In an associated intrazonal soil the uppermost 12 inches are black, smooth, highly dispersed clay, and the underlying material is light gray.

The red lateritic soils in this area have been farmed for centuries by the Huastecas Indians. Because of the rugged terrain, these soils are developed on slopes ranging from 45 to almost 100 per cent. Many of the slopes are too steep to allow cultivation and other tillage operations with animal power. Farming operations are accomplished largely by primitive hand tools. Cereals, vegetables, and other subsistence crops are grown. Although numerous exceedingly steep slopes are under cultivation there is very little erosion (pl. 1, fig. 2).

The lateritic soils in this region are developed from Cretaceous limestones.<sup>5</sup> The cover is a dense deciduous forest. A profile (pl. 1, fig. 3) observed 50 miles south of Tamazunchale, on a steep slope, illustrates the regional characteristics.

#### *Tamazunchale clay*

1. 0- $\frac{1}{2}$  inch, surface litter of deciduous tree leaves, mostly oak.
2.  $\frac{1}{2}$ -3 inches, dark reddish-brown clay with some organic matter.
3. 3-20 inches, red heavy clay, highly dispersed.
4. 20-48 inches, red smooth, heavy clay, highly dispersed.
5. 48+ inches, limestone.

The textural relations of the profile are shown in table 1. The first three horizons represent the residue derived from the fourth horizon of partially disintegrated Cretaceous limestone. As in most soils developed from limestone, these horizons are very high in clay and in colloid. The third layer contains 1 per cent sands, 3.6 per cent silt, and 94.5 per cent clay. The progressive increase in clay content downward suggests that some eluviation has occurred, but the relatively low clay and colloid content is due in part to incomplete dispersion of the dehydrated surface material. Most of the clay in all three horizons has probably remained in place, however, after the removal of calcium carbonate from the limestone by percolating water. Since this soil is developed on extremely steep slopes, a certain amount of erosion, creep, and slumping is apt to occur. Nevertheless, the data do not indicate that such action has occurred to any great extent in the profile examined, and if it has, profile adjustments appear to have been immediate.

The chemical analyses of the soil, table 2, suggest that the limestone residue has also undergone some decomposition and translocation. Silica and titanium decrease and the sesquioxides increase with depth. The complete loss of carbonates shows the thoroughness of the leaching throughout the profile

<sup>5</sup> Based on Geologic Map of Mexico by Willis (23) and Sanchez (19).



horizons. In spite of leaching, the surface horizon has been materially enriched in calcium, as is usual in soils derived from limestones. As a result of this enrichment the surface layer is less acid than the horizon immediately below it or even the one in direct contact with the limestone.

The analyses of the colloids are shown in table 3. The horizons show an increase in silica and alumina from the surface downward. Iron and titanium compounds tend to accumulate in the colloid of the upper layers. Sodium is thoroughly leached from the colloids, but the organic matter has doubtless retained the greater part of the magnesium, calcium, phosphorus, and sulfur in spite of thorough leaching of the profile.

The derived data, table 4, explicitly indicate the character of the colloids of the profile. The ratios show, for the most part, that the colloid is essentially the same for each horizon. The silica-sesquioxide, silica-iron-oxide, and silica-alumina, as well as the iron oxide-alumina, ratios, are low, approximating those of many of the colloids of lateritic soils in the United States. These ratios are about one-half as great as those of the parent material, high in limestone. For the parent material the ratios of silica to the sesquioxides, to the iron oxide, to alumina, and to the bases are 3.34, 25.00, 3.85 and 1.54, respectively. It seems evident that as compared to iron oxide and alumina one-half of the silica of the colloid has been lost in the formation of this colloid. The differences shown in the silica-total base ratios are not significant of large differences in in the soil colloid, since the colloids are so highly leached.

In general the data for this soil are very similar to those reported by Alexander, Edgington, and Byers<sup>6</sup> for soils in the United States which are derived from limestone. These data are also comparable to those of lateritic soils from various parts of the United States (4, 8, 14, 18) that are derived from granite and other parent materials. The soil, then, is a lateritic soil, but the presence of limestone as its base suggests a relationship to the terra rossa soils of Europe, some of which are lateritic red soils.

In view of these comparisons it is evident that the colloid of a soil, whether derived from limestone, granite, or other parent material, eventually has approximately the same composition if leaching, hydrolysis, and other soil-forming processes have been sufficiently active. The order of change is not precisely outlined by the data at hand, but it seems certain that only after the alkalinity is lowered by the complete removal of limestone from the soil by leaching are the remaining silicates destroyed by the same processes, but under more acid conditions, to form a lateritic soil much like the Cecil, Davidson, and others whose parent materials are not limestone.

#### *Podzolic and alpine meadow soils*

An interesting soil zonation like that described by Thorp (21) is found on the slopes of the Navado de Toluca, a mountain of volcanic origin 60 miles southwest of Mexico City. The summit, which is capped with snow throughout

<sup>6</sup> A chemical study of some soils derived from limestone. In manuscript, to be published as a U. S. Department of Agriculture Technical Bulletin.

most of the year, reaches an elevation of approximately 15,000 feet. This is 7,500 feet above Mexico City and 6,500 feet above Toluca, which is only a few miles distant. Vegetation ranges from short grass and brush near Toluca through fir on the lower mountain slopes, pine at higher elevations, and grasses above the timber line, to mosses on the nearly barren slopes above.

Soils range from brown soils near Toluca through podzolic soils on the lower mountain slopes and profiles having some features, at least, of podzols (pl. 1, fig. 4) at higher elevations, to alpine meadow soils developed under the grass vegetation above the timber line.

#### GENERAL DISCUSSION

The Mexican soils that have been described all have their counterparts in the United States. The similarity applies both to profile development and to chemical character of the colloidal materials. The Torreon profile is similar

TABLE 5  
*Review of Derived data\*: Mexican soil colloids*

SOIL TYPE	$\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3}$	$\frac{\text{H}_2\text{O}}{\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{H}_2\text{O}}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{TOTAL BASES}^\dagger}$	COMBINED WATER OF THE SOIL ACID†
Torreon sandy clay loam . . . . .	3.93	2.24	4.90	2.78	6.63	9.46
Juarez clay . . . . .	3.99	2.85	5.25	3.74	4.45	10.80
Agua Nueva sandy loam . . . . .	4.68	3.20	6.09	4.15	4.57	11.57
Irapuato clay loam . . . . .	3.12	2.27	3.99	2.90	7.56	11.39
Queretaro clay . . . . .	3.41	2.31	4.15	2.81	9.66	11.03
Tamazunchale clay . . . . .	1.61	1.89	1.92	2.26	40.08	13.24

\* Profile averages.

† Oxides of Mg, Ca, K, and Na.

‡ Water of combination plus the water equivalent of the bases, corrected for organic matter and carbonate content.

to the Phillips (5) of Montana. The Juarez and Agua Nueva profiles are high in soluble salts like the Fargo (5) of Minnesota. The Irapuato and Queretaro profiles are comparable to the Certe and Hastings (5) in Nebraska and to other chernozem profiles found elsewhere in the United States. The Tamazunchale profile bears a close resemblance to the lateritic Davidson and Cecil (18) and Decatur and Greenville profiles of the southeastern part of the United States.

In order to present certain characteristics of the soil colloids and to indicate the probable clay minerals formed in these soils under certain soil-forming processes, table 5 has been prepared. In this table only the profile averages are presented, since no extreme differences in composition are noted in the complete profiles.

The clay minerals are aluminosilicates that may be formed under a variety of conditions, but under certain comparatively restricted natural conditions they may be obtained pure. Their chemical and physical characteristics are

sufficiently certain to assure their mineralogical identity. The acids of these minerals are assumed to be montmorillonitic acid  $6\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , pyrophyllitic acid  $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , halloysitic acid  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . In these, iron doubtless more or less replaces alumina.

Because of the similarity of properties it is assumed that the clay minerals are present in soil colloids. Byers (6) has outlined their probable origin in soils essentially as a metathetical reaction between water and orthoclase or certain other reactive minerals. In the soil the soluble products of the reaction are removed by leaching, leaving the residual soil colloid, the composition of which is dependent on the intensity of the reaction and the degree of leaching.

The soils presented have been developed under varied rainfall. Although the character of the parent material, vegetation, and variations in temperature have influenced their formation, differences in the soil colloids may be ascribed chiefly to variations in moisture. Drainage has also modified the kind and character of the soil colloids.

The Torreon sandy clay loam has received the least rainfall of this group of soils, and the colloids throughout this profile might be expected to have been least altered. They are. The ratio of silica to sesquioxides is close to 4, and to alumina it is nearly 5, and the ratios of water to sesquioxides and to alumina are 2.24 and 2.78. The formula ratios then are  $3.93 \text{SiO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 2.24 \text{H}_2\text{O}$ ; and freed of iron, the ratio is  $4.90 \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2.78 \text{H}_2\text{O}$ . Iron is doubtless combined, in part at least, in the clay minerals where moisture is limited. The clay mineral in the gray desert soil, therefore, would be expected to approach the formula of pyrophyllitic acid,  $4 \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ . The combined water is low, 9.46 per cent. If no water, then, had been lost by dehydration under desert conditions it would be expected to approach more nearly the theoretical value of 13.6 per cent.

The limited drainage of the saline soils, Agua Nueva sandy loam and Juarez clay, does not permit the free removal of the products of the reaction of the soil minerals and water. Ordinarily, pyrophyllitic acid occurs only where there is free drainage. Nevertheless, the ratios of the Juarez clay closely approach the theoretical proportions for pyrophyllitic acid if iron is combined in the clay. A little better drainage at high alkalinity in the Agua Nueva sandy loam has caused a loss of alumina in proportion to silica. Theoretical proportions of the three major constituents are therefore not expected.

In the chernozem area the rainfall is greater than that in the area of gray desert soil. This would doubtless cause greater loss of bases and of silica and consequent hydrolysis of the combined iron of the clay, and therefore the clay minerals would be more highly aluminous. They are. Perhaps iron is partially combined, but if not, the formula ratios also closely approach the 4:1:3 ratio of pyrophyllitic acid.

For the lateritic Tamazunchale clay, rainfall is more than 100 inches, and extreme hydrolysis would be expected. Free iron oxide is indicated by the color of the soil and of the colloid. Its importance, therefore, in the silicate mineral would be still less than in the chernozems. Again ignoring any com-

bined iron, the formula ratio becomes  $1.92 \text{ SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2.26 \text{ H}_2\text{O}$ . The proportions of silica and alumina closely approach the values for halloysitic acid, the combined water is low, 13.24 per cent instead of the theoretical value of 19.6, but dehydration of the clay minerals is expected unless the temperatures are low or other conditions are particularly favorable for water retention.

Differences in the vegetation supported by these soils influence the character of the colloids. But the effects of the vegetation, kind and quantity, are so intimately bound with, and dependent on, the climatic conditions of each area in which one of the great soil groups has developed that the separate evaluation of their importance will not be attempted here. This has been discussed by Kellogg (11). It may be noted, however, that the low rainfall of the desert limits the vegetation of, as well as the removal of the bases from, the gray desert and associated azonal soils. The grasses have maintained the bases in the chernozem soils in spite of a higher rainfall than that found in the desert, but losses do occur. Extremely high rainfall has removed the limestone of the parent material, depleted the bases, caused extreme hydrolysis, and changed the character of the clay minerals of the lateritic Tamazunchale clay. Likewise, the vegetation is different. Instead of the scanty stunted shrub vegetation of the desert soils and the grasses of the chernozems, the lateritic soil favors the growth of coniferous and deciduous trees. Vegetation has its effect in soil formation, but the data at hand do not permit quantitative evaluation.

#### SUMMARY

Soil profiles occurring in northern and central Mexico are described. Chemical analyses are given of the soil horizons and their colloids present in six profiles which belong to four of the zonal and intrazonal soils.

These six soils have their counterparts in the United States, with respect to both profile development and character of colloid present.

In Mexico the great soil groups are represented in a comparatively limited area. This is due to the great differences in local relief and the attendant differences in climate and vegetation.

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## PLATE 1

### SOME SOILS OF MEXICO

FIG. 1. Chernozem profile in excavation south of Irapuato, Guanajuato, showing the unusual depth of the dark colored soil.

FIG. 2. Cultivated fields on steep slopes in the laterite soils region south of Tamazunchale, Potosi. Note the absence of gullies and erosion.

FIG. 3. Profile of a laterite soil south of Tamazunchale, Potosi, showing the steep slopes on which the laterite soils are developed, and also the dense forest in this region.

FIG. 4. Profile showing unusually deep organic A<sub>1</sub> horizon at an elevation of approximately 13,000 feet on Navado de Toluca. This profile has some of the features of a podzol.

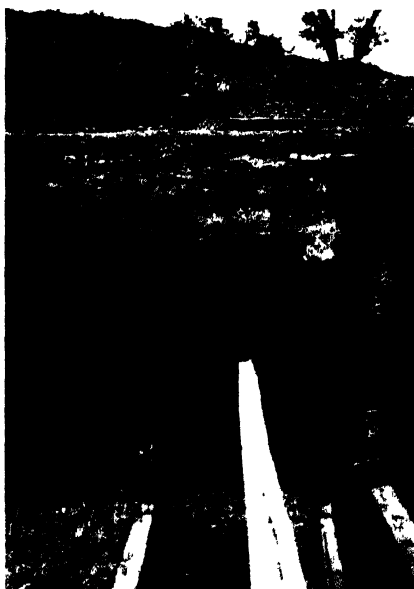


FIG. 1



FIG. 2



FIG. 3



FIG. 4



# THE MOVEMENT AND FIXATION OF SUPERPHOSPHATE IN SOILS

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The application of superphosphate to soils gives rise to several problems, all of which have reference to the profitable utilization of this valuable ingredient. The problems of crop response, uptake by plants, and like matters do not concern us directly in this investigation, which was undertaken primarily to discover what becomes of superphosphate when applied to a soil in its natural state. Such problems as the fixation of phosphate in less soluble forms and the possible loss by leaching will be dealt with as a matter of course, since they have particular reference to the work undertaken in the preparation of this paper.

## REVIEW OF LITERATURE

It is generally accepted that phosphoric acid is not subject to loss by leaching to any important degree. Thus Barker (1) says:

The movement of water through the soil gradually takes the phosphoric acid deeper into the soil, but the movement is so slow that for practical purposes it may be disregarded, except possibly on a light sandy soil subject to heavy rainfall and where the phosphoric acid is applied in its most soluble form, i.e. ammonium phosphate.

At Rothamsted (13) it is possible to account for nearly all the phosphate added during the last 70 years; some has gone into the crop, and nearly all the remainder is still in the soil, only very small quantities having been washed away. Gardner (9) states that "phosphates do not wash out in the drainage water, and are, therefore, not lost during wet conditions." Weir (19) points out that "movement of phosphorus to lower depths is usually very slow." This appears also to depend on the type of phosphate added, since, as Midgley (12) and later Spencer and Stewart (14) showed, phosphorus applied as disodium phosphate penetrated the soil more readily than did that applied as superphosphate or Ammo-Phos B. Superphosphate, according to Midgley (12), remained mostly in the surface inch of the soil, even after an interval of 6 months.

Stephenson and Chapman (15), however, found that in light- to medium-textured soils an appreciable penetration takes place below the surface foot, though they found little or no penetration to have taken place in very heavy

<sup>1</sup> Publication authorized by the director.



soils. They also found that in nearly all the soils receiving phosphate over a period of years there was a marked accumulation in the surface 6-12 inches. Single heavy applications of a soluble phosphate generally result in deeper penetration than that resulting from frequent small applications. Weidemann (18) pointed out that repeated applications of small amounts of phosphorus failed to increase the amount of available phosphorus in the soil. He also found that about 400 pounds of 20 per cent superphosphate per acre was required to produce a measureable increase in the amount of readily available phosphorus in the soil. That no movement of phosphate takes place except by erosion and crop uptake was the conclusion of Van Alstine (17). Were no movement to take place, obviously a fairly deep application of this ingredient would be advisable to bring it within the root zone. Such would appear to be the case in heavy soils. Midgley (12) found that the total increase of bluegrass resulting from superphosphate worked into the soil was 71.5 per cent greater than that from a mere surface application. Dyer (8), Midgley (12), and others refer to the increased penetration of phosphate when applied in conjunction with certain other salts. This is particularly the case with sodium nitrate, which would thus appear to be of more value when used in conjunction with superphosphate as a top dressing. It may be noted, however, that Brown (4) found no increased penetration resulting from the addition of sodium nitrate with the superphosphate, though the nitrate speeded up the penetration of rock phosphate in an acid soil.

Heck (10) found a penetration of water-soluble phosphorus through 5 inches of silt loam under laboratory conditions. He added, however, that under actual field conditions the same soil would allow much less penetration. It has been noted by Stephenson and Chapman (15) and by Spencer and Stewart (14) that phosphate associated with organic matter penetrates deeper than that in the inorganic form, and the latter writers have demonstrated that certain organic phosphates escape to a marked degree the fixation which occurs with phosphorus applied in some inorganic forms.

Brown (4) found that very little superphosphate remains available in the soil, and none of it penetrates deeper than 2 or 3 inches over 16 years. Rock phosphate applied in the same manner penetrated more than 7 inches. He notes that in most field trials superphosphate, nevertheless, has proved to be the better phosphorus fertilizer. The penetration of rock phosphate is confirmed by Thor (16), who found a marked penetration to a depth of 7-14 inches in a compact soil. Hockensmith, Gardner, and Kezer (11) found that in a calcareous soil triple superphosphate did not penetrate below the depth at which it was placed. Their experiments show that the depth of application makes a marked difference in the yield of alfalfa, 4-6 inches being the optimum depth of application. De Vries and Hetterschij (6), contrary to most other investigators, found fairly considerable penetration and leaching of superphosphate in two representative soil types studied by them.

## PLAN OF STUDY

In laying out an experiment to ascertain the movement and fixation of superphosphate, consideration must be given to soil type, involving mechanical and chemical composition and reaction; to method of application of the superphosphate; and to other factors such as application of water and topographical features.

Of the several distinct soil types existing on the Natal coast, two were selected because of their occurrence on the land allocated to the experiment station, where the work was carried out. Experiment 1 was laid out on dark heavy loam derived from a basic igneous intrusion known as dolerite; and experiment 2, on light sandy loam passing into slightly more compact material. In the latter soil type, at a depth of approximately 1 foot is a layer of pisolitic iron gravel or murrum, about 3 inches thick, below which is silty clay, passing into weathering Ecca shale. This soil type, which is very common in the sugar belt, is a very difficult soil to work on. Drainage is poor, and the compact layer of iron gravel (70 per cent  $\text{Fe}_2\text{O}_3$ ) largely inhibits root penetration. It is believed that the formation of the iron gravel is a result of the leaching down of iron salts. Eventually this layer tends to cement, forming a hard material known as "ouklip."

Each experiment was laid out in three 100-square-foot plots, each of which received a dressing of 800 pounds of superphosphate per acre. This was applied to the surface of plots 1 and 2 and at a uniform depth of 6 inches to plots 3. To effect the applications to plots 3 the soil was removed, replaced, and rolled level. Plots 1 were watered at intervals; plots 2 and 3 were not watered. The experiment thus involved three methods of application: (a) top dressing under irrigation, (b) top dressing without irrigation, (c) covering in—a common method in the planting of sugar cane—without irrigation. Irrigation, if copious immediately after fertilization, would naturally tend to wash the phosphoric acid into the soil. Irrigation in the present experiments, however, was light. This fact would account for its not having produced any significant movement of the phosphoric acid. Crawley (5) found that with immediate irrigation virtually all the phosphorus in a soluble phosphate was left within 6 inches of the surface, and that deferring of the irrigation for 15 hours halved the penetration.

Experiment 1 was studied in four layers; namely, 0–1 inch, 1–3 inches, 3–7 inches, and 7–12 inches. Experiment 2 was studied similarly except that an additional layer containing that of the iron gravel, 12–18 inches, was included. The layer 3–7 inches thus includes the superphosphate dressing of each plot 3. The mechanical composition of the various layers is given in table 1. The estimations were made by the Robinson pipette method with the modification proposed by the writer (2).

The fertilizer was added in a thin uniform layer obtained by weighing out the required portion for each square foot and sprinkling through a wire sieve.

A light application of water was added immediately to settle the fertilizer in case of disturbance by wind. The experiments were laid down in open fields surrounded by a fence, and they were thus exposed to the weather. It is somewhat unfortunate that during the period of this investigation four severe

TABLE 1  
*Physical composition of the soils*

DEPTH OF SOIL SAMPLE	COARSE SAND	FINE SAND	SILT	CLAY	MOISTURE	DISSOLVED MATERIAL	DIFFERENCE*
<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>Experiment 1</i>							
0-1	11.5	20.6	17.3	45.4	4.8	0.6	0
1-3	7.7	19.2	18.0	47.7	5.4	0.5	1.5
3-7	8.1	18.2	17.4	48.0	8.3	0.5	0
7-12	6.6	16.6	19.3	51.0	8.0	0.7	0
<i>Experiment 2</i>							
0-1	22.7	54.6	6.2	12.1	1.9	0.3	2.2
1-3	19.7	56.0	6.9	12.8	2.5	0.2	1.9
3-7	22.3	56.0	6.5	11.6	2.1	0.3	1.2
7-12	22.8	54.6	6.2	12.4	1.6	0.2	2.2
12-18	47.0	30.5	4.8	14.1	4.0	0.2	0

\* Including organic matter.

TABLE 2  
*Periods of sampling and amounts of rainfall*

SAMPLES	DATE OF SAMPLING	INTERVALS BETWEEN SAMPLINGS	TOTAL TIME FROM BEGINNING OF EXPERIMENT	PRECIPITATION	
				Plot 1*	Plots 2 and 3
		<i>days</i>	<i>days</i>	<i>inches</i>	<i>inches</i>
Immediately on application	Feb. 22, 1937	...	0	.....	.....
Series {	1 Mar. 8, 1937	14	14	1.33	0.23
	2 Apr. 2, 1937	23	37	2.84	2.04
	3 May 7, 1937	36	73	3.69	3.69
	4 July 2, 1937	57	130	3.56	1.66
	5 Sept. 13, 1937	72	202	3.96	3.21
	6 Mar. 5, 1938	173	375	26.97	26.82
Total.....				42.35	37.65

\* Including 4.70 inches applied.

rainstorms occurred, the precipitation in each case being over 2 inches. Losses due to such erosion are taken into account, however, in the interpretation of results.

Table 2 gives some preliminary information on the experimental work. It

will be noted that in addition to the analyses made immediately after application, six series of analyses were made over a period of 1 year.

#### SAMPLING AND METHODS OF ANALYSIS

Samples were taken by cutting away the respective soil layers from the entire length of the plot. Great care was observed in this process, and before each series was taken a section of soil about 8 inches wide was removed to

TABLE 3  
*HCl*\*-soluble  $P_2O_5$  in soil of experiment 1 (heavy soil type)

Results expressed in parts per million of soil

DEPTH	BEFORE APPLICA- TION	IMMEDI- ATELY AFTER AP- PLICATION†	SERIES 1, AFTER 14 DAYS	SERIES 2, AFTER 37 DAYS	SERIES 3, AFTER 73 DAYS	SERIES 4, AFTER 130 DAYS	SERIES 5, AFTER 202 DAYS	SERIES 6, AFTER 375 DAYS
<i>inches</i>								
<i>Plot 1</i>								
0-1	720	1,096	1,081	1,081	1,001	941	889	889
1-3	700	700	736	768	760	880	800	780
3-7	664	664	720	720	760	780	760	760
7-12	500	500	536	480	520	480	450	480
<i>Plot 2</i>								
0-1	720	1,096	1,067	1,040	1,000	800	760	760
1-3	700	700	889	889	800	712	720	752
3-7	664	664	752	680	696	680	660	720
7-12	500	500	432	440	456	480	400	464
<i>Plot 3</i>								
0-1	720	720	730	760	740	720	760	720
1-3	700	700	720	720	760	712	736	720
3-7	664	800	800	800	800	800	889	889
7-12	500	500	400	400	384	440	424	464

\* Sp. gr. 1.115.

† The amount theoretically present in plots 1 and 2, 0-1 inch, is 1,149 p.p.m., and that in plot 3, 3-7 inches, is 781 p.p.m. Both results are guided by the weight of soil (as calculated from the weights of an area 1 foot square), and cannot be strictly accurate.

eliminate any possible contamination of the layers by superphosphate that might have been washed down the sides. The samples were subsampled, air dried, again subsampled, passed through a 1-mm. sieve, and stored away in screw-cap bottles for analysis as soon as possible.

Three determinations were made on each sample; namely, total, available, and water-soluble phosphoric acid.

Total phosphoric acid was determined by refluxing 4 gm. of soil with 40 ml. HCl (sp. gr. 1.115) for 1 hour. Five milliliters of the filtrate was then evaporated

in the presence of calcium acetate solution, ignited, and extracted with 5 ml. of 10 per cent sulfuric acid. Phosphoric acid was determined colorimetrically on this extract. As a check on this estimation, several sodium peroxide fusions were made. The agreement was found to be close. Available phosphoric acid was determined by refluxing 10 gm. of soil with 100 ml. of 1 per cent citric acid for half an hour, igniting, and extracting as above. This procedure replaces the laborious method of shaking the soil in an end to end shaker, and has been found to be equally effectual. Water-soluble phos-

TABLE 4  
*Citric\*-soluble  $P_2O_5$  in soil of experiment 1 (heavy soil type)*

Results expressed in parts per million of soil

DEPTH	BEFORE APPLICA- TION	IMMEDI- ATELY AFTER AP- PLICATION†	SERIES 1, AFTER 14 DAYS	SERIES 2, AFTER 37 DAYS	SERIES 3, AFTER 73 DAYS	SERIES 4, AFTER 130 DAYS	SERIES 5, AFTER 202 DAYS	SERIES 6, AFTER 375 DAYS
<i>inches</i>								
<i>Plot 1</i>								
0-1	36	104	100	94	89	90	49	36
1-3	34	34	60	53	36	37	32	34
3-7	36	36	48	48	40	32	28	32
7-12	28	28	36	36	32	31	18	20
<i>Plot 2</i>								
0-1	36	104	76	70	92	80	52	37
1-3	34	34	36	33	44	38	34	29
3-7	36	36	31	53	32	30	24	29
7-12	28	28	21	45	35	24	16	17
<i>Plot 3</i>								
0-1	36	36	40	46	38	36	34	38
1-3	34	34	40	34	40	40	32	37
3-7	36	88	60	62	52	44	40	40
7-12	28	28	26	37	32	24	16	24

\* One per cent citric acid.

† The amount theoretically present in plots 1 and 2, 0-1 inch, is 455 p.p.m., and that in plot 3, 3-7 inches, is 150 p.p.m.

phoric acid was determined by leaching 100 gm. of soil in a Büchner funnel under vacuum with 500 ml. distilled water. Of this leachate, 100 ml. was evaporated, ignited, and extracted as above. With regard to this estimation, it has to be noted that dilution affects the solubility of soil phosphates. Dukes (7) found that, regardless of soil texture and content of phosphorus, the concentration of phosphorus in the soil solution increases on dilution for a time and then gradually decreases with further dilution. It is estimated that the above process of leaching, carefully controlled to take place in about 15 minutes, removes almost all the water-soluble phosphates.

## RESULTS

The results are given in tables 3-8 in parts per million of  $P_2O_5$ . A further interpretation will be given to them in a later part of this paper, particularly in respect to the amount of phosphate rendered unavailable by time.

The superphosphate used in these experiments was of extra high grade containing 20 per cent water-soluble, 20.5 per cent citric-soluble, and 21 per cent total  $P_2O_5$ .

TABLE 5  
*Water-soluble  $P_2O_5$  in soil of experiment 1 (heavy soil type)*

Results expressed in parts per million of soil

DEPTH	BEFORE APPLICA- TION	IMMEDI- ATELY AFTER AP- PLICATION†	SERIES 1, AFTER 14 DAYS	SERIES 2, AFTER 37 DAYS	SERIES 3, AFTER 73 DAYS	SERIES 4, AFTER 130 DAYS	SERIES 5, AFTER 202 DAYS	SERIES 6, AFTER 375 DAYS
<i>inches</i>								
<i>Plot 1</i>								
0-1	1.6	104.2	3.6	3.3	6.4	6.0	5.4	3.0
1-3	1.6	1.6	1.7	2.0	1.5	1.2	1.3	1.8
3-7	1.5	1.5	1.8	1.8	1.8	1.4	1.2	2.9
7-12	1.8	1.8	2.2	2.0	1.3	1.1	1.3	2.1
<i>Plot 2</i>								
0-1	1.6	104.2	4.7	4.0	6.6	5.6	4.0	2.2
1-3	1.6	1.6	1.5	2.6	1.3	0.7	1.3	2.2
3-7	1.5	1.5	2.0	1.4	2.5	1.2	1.6	2.5
7-12	1.8	1.8	2.0	2.8	2.7	1.0	1.4	1.3
<i>Plot 3</i>								
0-1	1.6	1.6	1.6	1.6	1.0	0.6	1.2	1.2
1-3	1.6	1.6	1.4	1.3	1.4	0.7	1.4	1.6
3-7	1.5	6.0	1.8	1.8	2.2	1.8	2.8	2.1
7-12	1.8	1.8	1.9	0.8	1.7	1.2	1.4	1.2

† The amount theoretically present in plots 1 and 2, 0-1 inch, is 410.2 p.p.m., and that in plot 3, 3-7 inches, is 112.9 p.p.m.

## INTERPRETATION OF RESULTS

*Total phosphate*

The first point to be noted about the figures in tables 3 and 6 is that there is a gradual loss of  $P_2O_5$  from the surface of the soil. As this is not accumulating in the soil of the next layer, it can safely be stated that the loss is due to erosion. To avoid the unnecessary complications arising from such losses, any future experiments of this nature could wisely be carried out under cover. In both experiments the loss from the plots receiving water is far less than that from the plots not watered during the initial stages. The loss on the dry plots is

almost double that of the watered plots in experiment 1, and it is exactly double in experiment 2. This is undoubtedly due to the bedding of the superphosphate by irrigation. The plots are on almost level ground and were kept free of weeds throughout the year.

That there is no noticeable increase in phosphate in any layer below 1 inch shows definitely that superphosphate does not penetrate the soil to any certain

TABLE 6  
*HCl*\*-soluble  $P_2O_5$  in soil of experiment 2 (light soil type)  
Results expressed in parts per million of soil

DEPTH	BEFORE APPLICA- TION	IMMEDI- ATELY AFTER AP- PLICATION†	SERIES 1, AFTER 14 DAYS	SERIES 2, AFTER 37 DAYS	SERIES 3, AFTER 73 DAYS	SERIES 4, AFTER 130 DAYS	SERIES 5, AFTER 202 DAYS	SERIES 6, AFTER 375 DAYS
<i>inches</i>								
<i>Plot 1</i>								
0-1	400	800	750	730	720	720	680	680
1-3	416	416	416	400	400	384	400	480
3-7	360	360	344	304	320	288	360	400
7-12	240	240	224	208	240	240	240	280
12-18	222	222	200	360	416	400	200	400
<i>Plot 2</i>								
0-1	400	800	720	608	560	544	560	560
1-3	416	416	416	384	360	360	400	400
3-7	360	360	328	336	304	304	320	344
7-12	240	240	240	240	272	240	296	224
12-18	222	222	200	256	270	320	200	368
<i>Plot 3</i>								
0-1	400	400	360	360	336	364	400	400
1-3	416	416	344	368	352	376	440	416
3-7	360	480	464	400	400	400	480	400
7-12	240	240	320	240	200	200	288	200
12-18	222	222	224	296	376	344	240	336

\* Sp. gr. 1.115.

† The amount theoretically present in plots 1 and 2, 0-1 inch, is 839 p.p.m., and that in plot 3, 3-7 inches, is 482 p.p.m.

degree. A slight increase may be noted in the 1-3-inch layer in several of the series, but as this is not constant, it may be concluded that such accumulation may have resulted from the phosphate's washing down cracks and fissures. The soil of experiment 1, where this increase is slightly more noticeable, showed many small cracks during dry weather. This accumulation extends, in some instances, down to 7 inches in experiment 1, but no such accumulation occurs in experiment 2 where the soil always remains compact, even though it is very

much lighter in texture and would be expected to have a tendency to retain far less phosphate than the soil of experiment 1. Below 7 inches no phosphate accumulates in experiment 1. In experiment 2 there are occasional abnormal accumulations in the gravel layer, but these are believed to have occurred through lateral infiltration, the phosphate having collected at the base of the experiment between successive samplings. It may be mentioned that in rainy

TABLE 7  
*Citric\*-soluble  $P_2O_5$  in soil of experiment 2 (light soil type)*

Results expressed in parts per million of soil

DEPTH	BEFORE APPLICA- TION	IMMEDI- ATELY AFTER AP- PLICATION†	SERIES 1, AFTER 14 DAYS	SERIES 2, AFTER 37 DAYS	SERIES 3, AFTER 73 DAYS	SERIES 4, AFTER 130 DAYS	SERIES 5, AFTER 202 DAYS	SERIES 6, AFTER 375 DAYS
<i>inches</i>								
<i>Plot 1</i>								
0-1	75	400	392	200	360	340	200	200
1-3	56	56	80	80	89	89	89	89
3-7	48	48	44	36	48	48	54	89
7-12	24	24	20	18	20	19	64	32
12-18	20	20	14	20	20	16	16	22
<i>Plot 2</i>								
0-1	75	400	220	180	160	200	184	200
1-3	56	56	80	89	48	48	48	64
3-7	48	48	40	46	40	40	44	60
7-12	24	24	14	16	20	24	50	26
12-18	20	20	14	16	18	16	24	20
<i>Plot 3</i>								
0-1	75	75	50	54	46	46	40	52
1-3	56	56	40	40	48	40	36	52
3-7	48	160	148	110	83	80	89	69
7-12	24	50	52	20	18	24	21	20
12-18	20	20	20	16	16	16	16	16

\* One per cent citric acid.

† The amount theoretically present in plots 1 and 2, 0-1 inch, is 504 p.p.m., and that in plot 3, 3-7 inches, is 167 p.p.m.

weather this gravel layer conducts a considerable amount of seepage water. This seepage was noted in the experimental plots. The conclusion drawn from this analytical work is that superphosphate does not penetrate below 1 inch, except in instances where ingress takes place through fissures in the soil. A further conclusion to be drawn is that superphosphate buried in the soil at a depth of 6 inches is not moved by soil water, as no loss takes place over 1 year from the layer sampled, namely, 3-7 inches.



The small variations occurring from one series to another are thought to be principally due to local variations in soil composition.

*Citric-soluble phosphate*

The study of available phosphate afforded an approximate means of distinguishing between loss of availability due to experimental procedure and that due to time. Far greater significance, of course, should be attached to

TABLE 8  
*Water-soluble  $P_2O_5$  in soil of experiment 2 (light soil type)*  
Results expressed in parts per million of soil

DEPTH	BEFORE APPLICA- TION	IMMEDI- ATELY AFTER AP- PLICATION†	SERIES 1, AFTER 14 DAYS	SERIES 2, AFTER 37 DAYS	SERIES 3, AFTER 73 DAYS	SERIES 4, AFTER 130 DAYS	SERIES 5, AFTER 202 DAYS	SERIES 6, AFTER 375 DAYS
<i>inches</i>								
<i>Plot 1</i>								
0-1	2.5	250.0	40.0	20.0	19.0	18.0	16.7	13.9
1-3	1.5	1.5	2.7	2.1	2.2	2.0	1.8	3.2
3-7	1.9	1.9	1.7	1.4	1.3	1.0	1.0	2.2
7-12	1.1	1.1	1.4	1.0	0.8	0.9	0.9	1.7
12-18	1.2	1.2	0.9	0.8	0.6	0.9	0.7	0.6
<i>Plot 2</i>								
0-1	2.5	250.0	27.8	13.0	7.2	8.0	14.3	11.9
1-3	1.5	1.5	2.4	1.2	0.8	0.9	1.0	1.8
3-7	1.9	1.9	2.1	1.4	0.9	1.0	0.9	1.2
7-12	1.1	1.1	1.1	1.0	0.8	0.9	0.8	1.2
12-18	1.2	1.2	0.8	0.6	0.6	0.9	0.9	0.9
<i>Plot 3</i>								
0-1	2.5	2.5	1.6	0.9	1.0	1.0	1.1	1.6
1-3	1.5	1.5	1.4	0.9	0.8	0.9	1.0	1.5
3-7	1.9	17.0	8.0	7.0	5.0	6.9	7.0	4.2
7-12	1.1	1.1	1.6	1.0	1.4	1.8	1.2	1.8
12-18	1.2	1.2	1.3	0.8	1.0	0.9	0.9	1.2

† The amount theoretically present in plots 1 and 2, 0-1 inch is 420.6 p.p.m., and that in plot 3, 3-7 inches, is 118.1 p.p.m.

fixation with time, since the experimental procedure creates optimum conditions for chemical (and physical) reaction which would not normally take place in the field. This is a fact generally disregarded in soil study, perhaps justly, since the difficulty is one which cannot readily be overcome. In experiment 1, 0-1 inch, 84 per cent of the loss of availability takes place immediately on application, and in the same layer of experiment 2, 24 per cent. In the 3-7-inch layer of experiment 1, this amounts to 54 per cent, and in the same layer

of experiment 2, it amounts to 6 per cent. The loss is roughly proportional to the clay content, as would be expected. The loss in the 3-7 inch layer is not entirely proportional to the loss in the 0-1-inch layer, probably on account of the different ratio of soil to phosphate solution, the 3-7-inch soil layer being four times as thick as the 0-1-inch layer for the same quantity of phosphate. These losses have, of course, taken place entirely during the analytical procedure and will have to be allowed for. The attempt to account for the loss of available phosphate in plots 1 and 2 and thereby the actual amount fixed in the soil was made by eliminating the two disturbing factors: first, mechanical transportation from the experiments by rainwater, wind, etc.; and second, amount of phosphate fixed in process of estimation. The assumption was that all the total phosphate lost was in the available form, since almost all the total phosphoric acid is in the available form in superphosphate.

The amount lost by mechanical means is easily determined, but the attempt to differentiate between the amounts fixed by process and by time was found to be impracticable. In plots 3, where the fertilizer was buried, less difficulty was experienced, as the complications arising out of mechanical losses did not occur.

As the subject of phosphate fixation comes to the fore in a consideration of the available phosphate left in the soil, reference to the writer's method of estimating phosphate fixation (3) is in order. This experimental procedure was adopted in attempting to ascertain fixation in the various series by adding to the control sample the amount of available phosphate estimated to be present for each series. The procedure is briefly as follows: 10 gm. of soil is refluxed with 100 ml. of 1 per cent citric acid containing 4 mgm.  $P_2O_5$  (as di-ammonium phosphate) for half an hour, and the amount of  $P_2O_5$  in solution is determined. From this is deducted the quantity of  $P_2O_5$  soluble in 1 per cent citric acid alone by the same process. The remainder, deducted, in turn, from the amount of available  $P_2O_5$  originally applied, gives the amount fixed in process.

In plot 3, the amount of available phosphate fixed by process could be arrived at by subtracting the amount immediately after application from the amount of phosphate originally present and added. If it is assumed that this will remain constant throughout the experiment, the amount fixed by time can be determined. Table 9 gives the results of this procedure.

From this table it may be noted that although the lighter soil has only about one-ninth of the fixing power of the heavier soil, the fixation occurs much more rapidly in the lighter soil. This is because initially almost twice as much phosphate is left available for fixation by time in the lighter soil.

The soil layers in both experiments were weighed and calculated to pounds per acre. The figures of series 6 in table 9, multiplied by 1.437, for experiment 1, and by 1.381, for experiment 2, will give the amounts fixed by time in pounds per acre 4-inch (3-7 inches).

Some objection to the final results of table 9 still remains. Since fixation

takes place with time, the available phosphate will decrease, and consequently the assumed constant amount fixed in process will probably decrease as well. The amounts fixed by time then would be too low and still not sufficiently representative of the degree of fixation by time. Table 9 shows, however, that a considerable part of the superphosphate buried in the soil remains available. It would appear from table 4 that all the fertilizer applied on the heavy type of soil has been fixed, but the fact that a large proportion can be fixed by process alone, throws doubt on such an assumption.

With respect to top dressing, unfortunately, little can be said, but it can be concluded that on sandy loam after 1 year, there still remains a considerable amount of available phosphate, whether applied in the drill or on the surface.

TABLE 9  
*Fixation of phosphate by time in soils of experiments 1 and 2*  
\* Results expressed in parts per million of soil

SERIES.....	1		2		3		4		5		6	
Period of time.....	After 14 days		After 37 days		After 73 days		After 130 days		After 202 days		After 375 days	
Experiment.....	1	2	1	2	1	2	1	2	1	2	1	2
Available $P_2O_5$ added and present	150	167	150	167	150	167	150	167	150	167	150	167
Available $P_2O_5$ found	60	148	62	110	52	83	44	80	40	89	40	69
Available $P_2O_5$ fixed by process and by time	90	19	88	57	98	84	106	87	110	78	110	98
Available $P_2O_5$ fixed by process*	62	7	62	7	62	7	62	7	62	7	62	7
Available $P_2O_5$ fixed by time	28	12	26	50	36	77	44	80	48	71	48	91

\* Obtained by deducting the amount of available  $P_2O_5$  immediately after application from the amount of available  $P_2O_5$  added and originally present.

#### *Water-soluble phosphate*

In experiment 1 all the citric-soluble phosphate remained water soluble in the process of estimation. A very rapid fall, however, is noted after 14 days, when the figure has reached its equilibrium. Thereafter for a year it varies only slightly. When the superphosphate is buried in the sand, almost all the phosphate is rendered insoluble in the process of estimation. This is very remarkable, as the experimental procedure involves only a 10-15 minute leaching of the soil with water; it goes to show the extreme rapidity with which phosphoric acid is absorbed by a clayey soil. After 14 days, no water-soluble phosphoric acid could be estimated in the soil. How much of this fixation is due to process and how much to time, it is not possible to say. An indication of the amount fixed by process can be obtained by reference to the quantity fixed immediately after application where process alone is the factor.

The lighter soil of experiment 2 was able to absorb less than half the water-soluble phosphoric acid in process, and an appreciable amount still remained after 14 days. After one year there was still about six times the original

amount of water-soluble phosphate found before application. The water-soluble phosphoric acid of buried superphosphate decreased very markedly in process, and after a year only about twice the original quantity was obtained.

If any movement of water-soluble phosphoric acid occurs, it is very slight. There is no penetration below the first inch in heavy soils, and only a very slight and erratic penetration in light soils.

These results show that in heavy soils after the application of 800 pounds per acre superphosphate, whether as a top dressing or in the drill, we cannot expect to find experimentally any water-soluble phosphoric acid at the end of a year. On lighter soils a small quantity remains unabsorbed, but such a statement would not be strictly accurate for fertilizer buried in this soil. It must be borne in mind, however, that though the results of experimental work show these to be the facts, greater quantities, nevertheless, occur in the soil in its undisturbed state. An attempt to estimate these quantities was made in the instance of available phosphate, but the only true indicator is the plant itself. That the citric-soluble and water-soluble phosphoric acid was rapidly absorbed by time has, nevertheless, been sufficiently demonstrated in these experiments.

#### SUMMARY AND CONCLUSIONS

A study was made of the movement and fixation of superphosphate under field conditions in two distinct soil types. This was ascertained by applying superphosphate as top dressing under irrigation, as top dressing without irrigation, in the drill and buried.

The study was conducted over one year, samples being taken at six intervals after application.

In these samples, total, citric-soluble, and water-soluble phosphoric acid were estimated.

The conclusions drawn from this work are as follows:

Erosion of total phosphate from surface dressings is considerable, being greater in the heavier soil type. In both soil types this has been very greatly reduced by watering. Movement of total phosphoric acid cannot be traced appreciably below the first inch from the surface, even in the lighter soil. Occasional penetration appears to take place in fissures. In neither the heavier nor the light soil has any loss from the buried superphosphate occurred. No movement below (or above) can be detected in the buried fertilizer.

Before results were interpreted an attempt was made to eliminate the effect of fixation by experimental procedure. This was not altogether satisfactory, but warranted the drawing of the following conclusions:

The fixation by analytical process in a heavy soil type is so much greater than that in a light soil as, perhaps, to obscure the results obtained. As a result, the fixation with time in a light soil stands out more clearly than that in a heavy type, although a heavier fixation in the heavy type actually takes place.

Watering tends to prolong somewhat the availability of phosphate.

Water-soluble phosphate is lost in considerable amounts in process of estimation in a heavy soil type, and in appreciable amounts in a lighter type. After 14 days virtually all the water-soluble phosphate has vanished from the heavy soil, but at the end of a year some still remains in the light soil, the loss being very gradual. In a heavy soil type the increase in water-soluble phosphate, due to applications of 800 pounds superphosphate per acre, is almost negligible, whether the dressing be applied in the soil or on the surface.

The fact that analytical results with respect to phosphate fixation can be very misleading if interpreted literally has been illustrated. Since the experimental procedure itself plays a disturbing part, such figures do not necessarily reflect conditions prevailing in the soil.

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## ACTION OF CARBON DIOXIDE ON SOILS

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Carbon dioxide plays an important rôle in the economy of nature. Not only is it the means of transport of carbon from one place to another, but by its acidic character it causes the movement of minerals, the weathering of rocks, and the release of plant nutrients from the soil. The reaction of natural soils, especially that of highly alkaline soils in which the pH value is entirely governed by the carbonate-bicarbonate ratio (3), is greatly modified by its buffer action. It is therefore of interest to study the action of  $\text{CO}_2$  on soils with particular reference to the nature and amount of exchangeable bases in them.

Two things seemed important in such an investigation: the control of the partial pressure of  $\text{CO}_2$  and the control of the nature and amount of exchangeable bases. The former was accomplished by the help of gas meters, and the latter by simply neutralizing an unsaturated soil with different bases up to various pH values. Air containing varying amounts of  $\text{CO}_2$  was passed through the soil suspensions held in a funnel with a sintered glass disk. The air containing  $\text{CO}_2$  was forced from the bottom, which kept the suspension well stirred. Preliminary observations showed that the results with  $\text{CO}_2$ -air mixtures of varying composition were erratic. The nature of the substances involved and the experimental technic do not admit of a graded reaction capable of measurement. Two standards were, therefore, adopted; namely 1 per cent  $\text{CO}_2$  and 100 per cent  $\text{CO}_2$ . The results recorded in this paper refer only to these concentrations.

### ACTION OF $\text{CO}_2$ ON THE SOLUBLE SALTS AND ON THE pH VALUE OF SOILS

The main effect of  $\text{CO}_2$  on soils, and the one that is of greatest interest from the practical point of view, is associated with alterations in the soluble salts and in the pH values. Twenty-five soils were used for this study. Only  $\text{CO}_2$  was passed through the suspension, which had a soil-water ratio of 1:10. The pH values were determined with the glass electrode. The results, given in table 1, show that the soluble salts increased and the pH value decreased. The extent of the change seems to be different for different soils. The ratio of the pH values before and after the passage of  $\text{CO}_2$  is, however, fairly constant (approximately 0.7) but is slightly higher for soils containing no  $\text{CaCO}_3$  than for calcareous soils. The ratio of soluble salts before and after  $\text{CO}_2$  treatment is not constant. There is some indication, however, that this ratio is higher

for carbonate-free soils than for those containing  $\text{CaCO}_3$ . If the lowering of the pH value is partly due to an increase in the soluble salts (1), then a certain degree of parallelism between the two ratios is comprehensible. The effect of  $\text{CO}_2$  on soluble salts is similar to that of soils. Results with a few salts are

TABLE 1  
*Effect of  $\text{CO}_2$  on pH and on soluble salts of soils*

SOIL P.C.	CLAY 0.002 MM.	CARBONATE	INITIAL pH ( $\text{pH}_1$ )	pH AFTER PASSAGE OF $\text{CO}_2$ ( $\text{pH}_2$ )	$\frac{\text{pH}_2}{\text{pH}_1}$	SALTS BEFORE PASSAGE OF $\text{CO}_2$ ( $\text{S}_1$ )	SALTS AFTER PASSAGE OF $\text{CO}_2$ ( $\text{S}_2$ )	$\frac{\text{S}_2}{\text{S}_1}$
	<i>per cent</i>	<i>per cent</i>						
1	11.30	34.25	8.08	5.70	0.70	0.26	0.75	2.88
2	59.35	5.0	7.90	5.64	0.71	0.42	0.66	1.57
3	62.2	0.5	7.37	5.22	0.70	0.078	0.40	5.12
4	15.2	1.0	8.48	5.6	0.66	0.11	0.5	4.54
5	12.3	1.87	8.8	5.9	0.67	0.078	0.66	8.46
6	28.4	0.0	5.42	4.25	0.78	0.26	0.70	2.69
7	21.8	6.5	9.46	5.8	0.61	0.93	1.8	1.93
8	25.2	0.75	7.7	4.7	0.61	0.13	0.44	3.38
9	21.6	0.0	5.6	4.4	0.78	0.084	0.15	1.78
10	35.6	1.12	7.9	5.2	0.65	0.198	0.73	3.68
11	32.8	2.5	7.5	5.2	0.69	0.18	0.93	5.16
12	7.2	0.0	5.9	4.1	0.69	0.27	0.36	1.33
13	58.9	1.5	7.5	5.0	0.66	0.16	0.54	3.37
14	21.5	0.0	5.57	4.8	0.86	0.05	0.18	3.60
15	22.4	0.25	7.14	5.1	0.71	0.28	0.45	1.60
16	8.7	1.87	7.6	5.35	0.70	0.20	0.66	3.30
17	14.1	0.5	7.3	4.8	0.65	0.30	0.49	1.63
18	22.6	0.12	5.62	4.48	0.79	0.09	0.15	1.66
19	42.6	1.0	7.27	5.22	0.71	0.22	0.44	2.00
20	8.1	0.12	5.74	4.32	0.75	0.07	0.14	2.00
21	13.5	2.87	7.2	5.4	0.75	0.22	0.68	3.09
22	15.1	0.12	5.9	4.74	0.80	0.11	0.23	2.09
24	9.7	1.75	7.32	5.42	0.74	0.13	0.82	6.30
25	4.0	0.0	5.8	5.8	1.0	0.05	0.29	5.80
26	22.5	0.0	6.4	5.8	0.79	0.16	0.29	1.81
Sodium acetate.....			7.6	5.77	0.75	....	....	...
Sodium baborate.....			8.86	6.66	0.75	....	....	....
Sodium urate.....			8.92	6.64	0.74	....	....	....
Sodium carbonate.....			10.7	6.92	0.65	....	....	....

included in table 1, and the ratio  $\text{pH}_2/\text{pH}_1$  is of the same order as in the case of soils.

#### ACTION OF $\text{CO}_2$ ON SINGLE-BASE SOILS

Single-base soils were prepared by treating a completely unsaturated soil with increasing quantities of various hydroxides. Carbon dioxide was passed

through suspensions of these soils. The results are given in table 2. It is seen that Na-soil is not flocculated by  $\text{CO}_2$ . This point will be discussed more fully later. At the lower pH values the flocculation is only partial. The ratio  $\text{pH}_2/\text{pH}_1$  decreases as the original pH increases irrespective of the nature of the exchangeable base in the soil.

TABLE 2  
*Action of  $\text{CO}_2$  on single-base soils at various pH levels*

SOIL	INITIAL pH ( $\text{pH}_1$ )	pH AFTER PASSAGE OF 1 PER CENT $\text{CO}_2$	pH AFTER PASSAGE 100 PER CENT $\text{CO}_2$ ( $\text{pH}_2$ )	FLOCCULA- TION*	pH AFTER ADDITION OF $\text{CaCO}_3$	pH AFTER PASSAGE OF $\text{CO}_2$	$\frac{\text{pH}_2}{\text{pH}_1}$
<i>m.e./100 gm.</i>							
K-Soil:							
39	5.75	5.55	5.18	F	6.45	5.83	0.90
51	7.2	5.8	5.6	F	6.6	6.27	0.77
77	9.83	6.8	6.06	F	7.55	6.53	0.61
Na-Soil:							
20	4.32	4.32	4.24	X	7.08	6.26	0.98
48	6.7	7.1	5.5	X	7.82	6.2	0.82
72	9.25	6.27	6.03	X	6.95	6.28	0.65
Ca-Soil:							
34	3.94	3.83	3.82	PF	No $\text{CaCO}_3$ added to calcium soil		0.96
56	5.97	5.8	5.8	F			0.97
96	9.6	6.8	6.1	F			0.63
Mg-Soil:							
34	5.5	4.5	4.6	PF	5.02	4.78	0.83
56	7.06	6.35	5.47	F	7.15	5.7	0.77
100	8.2	6.6	5.9	F	7.8	6.4	0.71

\* F = flocculated; PF = partly flocculated; X = no flocculation.

#### RÔLE OF $\text{CO}_2$ IN THE RECLAMATION OF ALKALI SOILS

The action of  $\text{CO}_2$  on soils at once raises the question of the rôle of  $\text{CO}_2$  in the reclamation of alkali soils. Alkali soils, as is well known, have the following characteristics:

- High exchangeable Na as compared to other bases, especially Ca.
- High pH value.
- A state of deflocculation or dispersion.

Reclamation of such soils naturally brings about a change in the reverse direction. We shall therefore see to what extent these changes can be brought about by  $\text{CO}_2$  in soils of varying degrees of alkalinity. Calcium carbonate is an important constituent of the majority of alkali soils; the action of  $\text{CO}_2$ , therefore, was studied with and without  $\text{CaCO}_3$ .

Soils of varying degrees of alkalinity at different pH levels were prepared by neutralizing the H-soil with varying quantities of  $\text{Ca}(\text{OH})_2$ -NaOH mixtures of appropriate strength. The results are expressed in terms of the percentage



of sodium in the total bases ( $\text{Ca} + \text{Na}$ ) present in each soil and are given in table 3. The following conclusions regarding the action of  $\text{CO}_2$  on soils are drawn as a result of this study.

There is a substantial decrease in the pH values at all degrees of alkalinity, as indicated by the percentage of  $\text{NaOH}$  in the mixtures of hydroxide.

At low pH values flocculation occurs at all degrees of alkalization. When the pH value is high, flocculation fails to take place at degrees of alkalinity higher than 60–80 per cent.

In the presence of  $\text{CaCO}_3$  a large quantity of exchangeable  $\text{Na}$  is brought into solution which could be leached out, resulting in a substantial reduction in the degree of alkalization.

TABLE 3  
*Effect of  $\text{CO}_2$  on soils of different degrees of alkalinity*

$\text{NaOH}$	$\text{Ca(OH)}_2$	DEGREE OF ALKA- LINITY	INITIAL pH ( $\text{pH}_1$ )	pH AFTER PASSAGE OF 1 PER CENT $\text{CO}_2$	pH AFTER PASSAGE OF 100 PER CENT $\text{CO}_2$ ( $\text{pH}_2$ )	FLOCCU- LATION*	pH AFTER ADDITION OF $\text{CaCO}_3$	pH AFTER PASSAGE OF $\text{CO}_2$	$\frac{\text{pH}_2}{\text{pH}_1}$
m.s./100 gm.	m.s./100 gm.	per cent							
0	12	0	5.80	6.02	5.2	F	....	....	0.89
1.6	6.4	20	5.86	5.67	5.26	F	6.58	5.77	0.89
3.2	4.8	40	5.86	5.86	5.4	F	6.47	5.86	0.92
4.8	3.2	60	5.95	5.8	5.4	F	6.4	5.85	0.90
6.4	1.6	80	6.0	5.86	5.25	F	7.0	6.0	0.87
8	0	100	6.5	5.5	5.25	F	6.9	5.9	0.80
0	18	0	6.0	6.38	5.02	...	....	....	0.83
3.2	12.8	20	6.2	5.55	5.4	F	6.32	5.85	0.87
6.4	9.6	40	6.4	6.2	5.4	PF	6.38	6.0	0.84
9.6	6.4	60	6.4	5.7	5.5	PF	6.43	5.87	0.85
12.8	3.2	80	6.6	5.36	4.58	PF	6.28	5.8	0.69
16	0	100	7.33	5.06	4.62	PF	6.38	5.9	0.63
0	50	0	8.3	7.55	5.8	F	....	....	0.69
8	32	20	8.6	7.5	5.6	F	6.9	5.8	0.65
16	24	40	8.8	6.17	5.6	F	6.6	5.8	0.63
24	16	60	9.1	7.35	5.78	PF	6.8	6.1	0.63
32	8	80	9.35	6.75	6.1	PF	7.54	5.9	0.65
40	0	100	9.5	6.5	6.0	X	7.2	6.18	0.64

\* F = flocculated; PF = partly flocculated; X = no flocculation.

The laboratory results are substantiated by a number of field observations on alkali soils. It was found that in a rice field the pH values of soil samples taken from near the roots were lower by more than 1 pH unit than that of the soil taken from some distance away. Similar results were obtained in a field under grass.

The importance of  $\text{CaCO}_3$  in the reclamation of alkali soils is well brought out. These results are in agreement with the observations of Puri et al. (2), who showed that the movement of  $\text{CaCO}_3$  in alkali soils causes their regeneration or reclamation. Calcareous soils are, therefore, more easily reclaimed than are carbonate-free soils.

Smith and co-workers have presented data (4) which apparently tend to show that  $\text{CO}_2$  may result in an increased pH value of the soil solution, depending upon the soil type. Their results would seem to contradict our observations, in which we have consistently found a lowering of the pH value as a result of the action of  $\text{CO}_2$ . The experimental technic of these authors was entirely different from ours. They used soil in plots to which  $\text{CO}_2$ -saturated water was added or to which  $\text{CO}_2$  was passed from below at the rate of 5 liters an hour for 1 hour each day throughout the experiment, which extended over several months. It was therefore not entirely the effect of  $\text{CO}_2$  that was being measured, but the cumulative effect of several factors not entirely under control. A solution of  $\text{CO}_2$  in water has a pH value of about 4; it is therefore bound to decrease the pH value of a soil on coming in contact with it. Secondary changes, which might raise the pH value, must take place, however, in the course of time.

#### SUMMARY

The action of  $\text{CO}_2$  on soils has been studied by following the changes in the pH values.

The importance of  $\text{CO}_2$  in the reclamation of alkali soils is well brought out by the observation that  $\text{CO}_2$  induces changes that are the reverse of alkalization.

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## COENZYME R REQUIREMENTS OF RHIZOBIA

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In previous publications (1, 2, 3, 7) from this laboratory it was shown that certain, but not all, species of *Rhizobium* require addition of the accessory growth substance, coenzyme R, in order for good growths to occur. Most strains of *Rh. trifolii*, *Rh. leguminosarum*, *Rh. meliloti*, and *Rh. phaseoli* tested show a 20- to 80-fold increase in growth within 4 to 6 days following additions of 0.5 to 1 p.p.m. of our more concentrated preparations. Organisms of the cowpea, soybean, and lupine groups usually make only a very limited response. Although the chemical and physiological studies strongly indicate that the growth response is due to one substance, it is possible that a group of substances, having similar chemical properties, may act as the essential factor.

Several investigators, especially Thorne and Walker (10), Clark (6), and McBurney, Bollen, and Williams (8), have confirmed these findings in major part at least. More recently, however, Thorne and Walker (11) reported data from which they concluded that "no evidence was found which indicates that the root nodule bacteria require any complex, unidentified substances for their growth. Many materials, however, are able to stimulate the growth and respiration of these organisms in mineral salts-sucrose c.p. media with KNO<sub>3</sub>, NH<sub>4</sub>Cl, or asparagin employed as sources of nitrogen." They arrived at this conclusion even though they obtained scarcely any growth of *Rh. trifolii* in a medium containing c.p. sucrose and potassium nitrate, but did obtain a 46-fold growth increase within 2 days after the addition of an alcoholic extract of commercial cane sugar, which, as Allison and Hoover (1) showed previously, contains coenzyme R in considerable quantities. With asparagin the total growth was greater, although the increase over the control was less, probably because of the trace of growth factor that is usually present as an impurity in asparagin unless it has been carefully recrystallized.

Thorne and Walker reported also that *Rh. meliloti* and *Rh. trifolii*, although unable to make good growths for several consecutive transfers on a c.p. sucrose-nitrate medium, were able to do so if asparagin or ammonium chloride was substituted for the nitrate. Furthermore, if small quantities of the reducing substances, cysteine or thioglycollic acid, were added to the nitrate medium,

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growth was satisfactory. Ferric chloride was also beneficial. They interpreted these results to mean that the inability of the rhizobia to make good growths for several transfers in the c.p. sucrose-nitrate-inorganic salts medium previously used in our laboratory is due to (a) deficient iron and (b) too high an oxidation-reduction potential in the presence of potassium nitrate. In our previous papers (1, 2, 3) special attention was given to iron, since we originally suspected that the accessory growth factor was available iron. It was concluded (2) that "the iron requirements of rhizobia are small. The stimulating effect of additions of available iron was usually less than 10 per cent in a synthetic medium prepared from c.p. ingredients." This iron effect is negligible in comparison with the 20- to 80-fold effect commonly obtained with coenzyme R preparations. Likewise, our work (3) showed that "reducing substances, such as cysteine, thioglycolic acid, and glutathione, do not in any degree act as substitutes for coenzyme R." In studies of nitrogen sources, ammonium chloride, ammonium nitrate, and ammonium sulfate usually gave poorer growths than potassium nitrate, and hence the latter was commonly used. As a nitrogen source, asparagin is as good as, and sometimes slightly better than, potassium nitrate, but it usually contains a trace of growth factor present as an impurity.

In view of the statements of Thorne and Walker (11), the present further investigations were made of the effect of altering the medium in the various ways mentioned by them. It was especially desired to determine whether such changes would make coenzyme R unessential to the growth of the strains of rhizobia that ordinarily appear to require its addition to the medium.

#### METHODS

The basal medium used had the following composition:  $K_2HPO_4$ , 0.8 gm.;  $KH_2PO_4$ , 0.2 gm.; NaCl, 0.2 gm.;  $MgSO_4 \cdot 7H_2O$ , 0.2 gm.;  $CaSO_4 \cdot 2H_2O$ , 0.1 gm.; and  $H_2O$ , dist., 1,000 cc. The two phosphate salts were dissolved first, and solutions of the other salts were then added. The medium was allowed to stand until the resulting precipitate had settled, and then the clear solution was siphoned off for use as needed. Iron was then added at the rate of 5 p.p.m., either as ferric chloride (tables 1-3) or as ferric sulfate (tables 4 and 5), and the precipitate that formed was allowed to remain. Sucrose, c.p., previously tested and known to be nearly free from coenzyme R, was usually supplied at the rate of 3 gm. per liter. This low concentration, which is adequate for heavy growths of rhizobia, reduces the quantity of growth factor added as impurity. Nitrogen was added, at the rate of 2.5 mgm. per 25 cc. of medium, in the form of potassium nitrate, ammonium chloride, or asparagin (recrystallized). Since this medium is saturated with respect to certain salts, 10 per cent additional water was added before autoclaving in order that it would remain clear. A little brom thymol blue was added in some cases where it was desired to observe the changes in pH during growth. Prior to inoculation the pH was approximately 7.2. All experiments were carried out in 250-cc. cotton-stoppered

Erlenmeyer flasks, containing 25 cc. of medium, and at a temperature of 28°C.

The coenzyme R preparation used in all experiments except that reported in table 5, was a concentrated acetone extract of an *Azotobacter vinelandii* culture medium (7).

The cultures of rhizobia used were obtained from I. L. Baldwin, University of Wisconsin; D. W. Thorne, Iowa State College; and A. I. Virtanen, Helsinki, Finland. The species, strain numbers, and sources are given in connection with each of the tables. Growth measurements are reported in terms of numbers of bacteria as determined by direct microscopic counts, using a Levy-Hausser bacterial counting chamber having a depth of 0.02 mm.

#### NITROGEN SOURCES

In table 1 are reported the results of growth experiments with three species of rhizobia, grown with ammonium chloride, potassium nitrate, and asparagin

TABLE 1

*Effect of coenzyme R on growth of rhizobia with different nitrogen sources*

(Millions of bacteria per cc. on 5th day)

TREATMENT	RH. TRIFOLII 205*	RH. MELLIOTI 131*	RH. LEGUMINO- SARUM 302*
NH <sub>4</sub> Cl .....	2.0	9.6	6.8
NH <sub>4</sub> Cl + 1.3 p.p.m. co. R.....	680.0	760.0	460.0
KNO <sub>3</sub> .....	9.2	9.8	....
KNO <sub>3</sub> + 1.3 p.p.m. co. R.....	1180.0	880.0	....
Asparagin .....	2.0	16.4	....
Asparagin + 1.3 p.p.m. co. R.....	1040.0	920.0	....

\* Cultures obtained from University of Wisconsin.

added to the basal medium in the presence and in the absence of the growth accessory substance. Each flask, containing 25 cc. of culture medium, was inoculated with 2 drops (900,000 organisms) of 3-day cultures grown on a medium containing very small amounts of coenzyme R.

The data of table 1 show that in the absence of coenzyme R scarcely any growth was obtained with the three cultures of rhizobia used. In the presence of 1.3 p.p.m. of the growth accessory substance, growth increases varying from 56- to 520-fold were obtained, irrespective of whether ammonium chloride, asparagin, or potassium nitrate was used as the nitrogen source. In the presence of coenzyme R, growth with ammonium chloride was definitely poorer than with either asparagin or potassium nitrate, because of the lower pH that developed with the chloride. This experiment shows, therefore, that the strains of rhizobia used were unable to make appreciable growths within 5 days on a medium containing adequate iron and the reduced forms of nitrogen suggested by Thorne and Walker, but deficient in coenzyme R. The data in

tables 2, 3, and 4, discussed in some detail below, show similar results. These data are also in agreement with those of Clark (6), who used ammonium chloride as a nitrogen source in his experiments.

#### EFFECT OF REDUCING AGENTS

The effects of additions of the reducing agents, thioglycollic acid and cysteine, on the growth of *Rh. trifolii* and *Rh. meliloti* in ammonium chloride and potassium nitrate media, and in the presence and absence of coenzyme R, are shown in table 2. The medium and the experimental procedure used were the same as those for the experiment reported in table 1. The thioglycollic acid was pipetted aseptically from the original bottle, neutralized with sterile KOH solution, and added to the medium after sterilization. The cysteine was sterilized separately in the autoclave before addition to the various flasks of sterile media. Each flask was inoculated with 2 drops (about 900,000 organ-

TABLE 2

*Effect of reducing agents on growth of rhizobia in presence and absence of coenzyme R*  
(Millions of bacteria per cc. in 4 days)

TREATMENT	RH. TRIFOLII 205*				RH. MELILOTI 131*			
	NH <sub>4</sub> Cl		KNO <sub>3</sub>		NH <sub>4</sub> Cl		KNO <sub>3</sub>	
	No co. R	Co. R	No co. R	Co. R	No co. R	Co. R	No co. R	Co. R
Control.....	1.4	780.0	9.6	680.0	8.0	540.0	9.8	660.0
Thioglycollic acid 0.01 per cent.....	1.4	720.0	7.0	680.0	7.6	600.0	10.2	680.0
Thioglycollic acid 0.002 per cent.....	1.4	780.0	38.0	700.0	..	620.0	12.8	700.0
Cysteine HCl 0.01 per cent.....	1.2	320.0	7.8	540.0	4.8	620.0	10.0	700.0
Cysteine HCl 0.002 per cent.....	1.2	780.0	6.2	700.0	6.2	640.0	11.0	840.0
Cysteine HCl 0.0004 per cent.....	1.4	800.0	6.8	660.0	9.6	620.0	11.6	700.0

\* Cultures obtained from University of Wisconsin.

isms) of a 5-day culture grown on a medium containing very small amounts of growth factor. The inoculations of the media containing ammonium-chloride were with organisms grown on ammonium chloride; likewise, organisms grown on KNO<sub>3</sub> were used to inoculate media containing KNO<sub>3</sub>.

Neither of the reducing agents, when added to a medium containing adequate iron and either ammonium-chloride or potassium nitrate, acted as a substitute for coenzyme R. The effects of both thioglycollic acid and cysteine, when added at nontoxic concentrations, were slight, both in the presence and in the absence of the growth factor, and with the two cultures of rhizobia. It is well to point out that in this experiment the numbers of organisms added in the inocula were fairly large, and hence the effect of reducing agents on initiation of growth with exceptionally small inocula, stressed by Allyn and Baldwin (4, 5), was not an important factor.

Further data on the effect of thioglycollic acid on the growth of 12 cultures

of rhizobia on asparagin and potassium nitrate, are given in table 3. The methods used were, for the most part, the same as those in the two preceding experiments. A little brom thymol blue to serve as a pH indicator was added. The quantity of inoculum used was much smaller, consisting of 1 loopful of a 2-day culture grown on a medium containing very little growth factor. Scarcely any growth was visible macroscopically in these 2-day cultures.

The striking effect of coenzyme R on the growth of the various species and strains of rhizobia both with asparagin and with potassium nitrate is shown in table 3. The inability of thioglycollic acid to act as a substitute for coenzyme R in the presence of abundant iron is also shown very clearly. By using a small

TABLE 3

*Response of various strains of rhizobia to coenzyme R in presence and absence of 0.002 per cent thioglycollic acid*

(Millions of bacteria per cc. in 5 days)

ORGANISMS*	KNO <sub>3</sub>				ASPARAGIN			
	No co. R		Co. R 1.3 p.p.m.		No co. R		Co. R 1.3 p.p.m.	
	No thio.	Thio.	No thio.	Thio.	No thio.	Thio.	No thio.	Thio.
<i>Rh. trifolii</i> 202.....	2.0	2.0	160.0	200.0	2.0	2.0	760.0	860.0
“ “ 205.....	7.0	7.4	660.0	780.0	2.0	1.8	640.0	640.0
“ “ 209.....	0.4	0.4	640.0	700.0	0.4	0.4	640.0	440.0
“ “ VI.....	1.4	1.4	420.0	440.0	1.0	1.0	440.0	400.0
<i>Rh. leguminosarum</i> 302.....	4.0	3.6	640.0	600.0	4.0	4.0	540.0	600.0
“ “ 310.....	1.0	1.0	660.0	620.0	1.0	1.0	620.0	660.0
“ “ 317.....	1.0	1.0	600.0	620.0	1.0	1.0	380.0	480.0
“ “ XX.....	1.0	1.0	300.0	300.0	1.0	1.0	640.0	680.0
<i>Rh. phaseoli</i> 402.....	1.0	1.0	460.0	400.0	1.0	1.0	1.0†	340.0
<i>Rh. meliloti</i> 101.....	0.4	0.4	80.0†	760.0	0.4	0.4	400.0	460.0
“ “ 131.....	10.0	9.6	820.0	880.0	5.0	6.0	900.0	880.0
“ “ 113.....	8.0	6.0	600.0	620.0	10.0	4.0	620.0	620.0

\* *Rh. trifolii* VI and *Rh. leguminosarum* XX cultures obtained from A. I. Virtanen, Helsinki, Finland; all other cultures obtained from University of Wisconsin.

† On the 7th day the numbers of bacteria in these flasks were about 60 per cent as large as those in the corresponding flasks to which thioglycollic acid had been added.

quantity of inoculum and a very pure sugar the essentialness of coenzyme R is made more evident.

Although thioglycollic acid did not act as a substitute for coenzyme R it did increase the growth of 2 of the 12 strains of organisms used. With one of these strains the favorable effect occurred in KNO<sub>3</sub> but not in the asparagin medium, whereas with the other organism the reverse was true. This favorable effect of thioglycollic acid may have been due to its effect on growth initiation where the inoculum is small. The numbers of organisms added in the inoculum varied for the 12 strains from less than 1,000 to about 5,000 per cubic centimeter of the final culture medium.



## SPECIES AND STRAINS OF RHIZOBIUM

The results given in tables 1-3 of tests with 4 species and a total of 12 strains of *Rhizobium*, which ordinarily make good growths on yeast extract media, show a close agreement as far as need for coenzyme R is concerned. Considering, however, that some of the results reported by Thorne and Walker (11), especially those in table 1 of their paper, appear to be in distinct disagreement

TABLE 4

*Growth of rhizobia on asparagin and potassium nitrate in presence and absence of coenzyme R*  
(Millions of bacteria\* per cc.)

NITROGEN SOURCE AND ORGANISMS†	TRANSFER NO. 1				TRANSFER NO. 2				TRANSFER NO. 3			
	No co. R		Co. R		No co. R		Co. R		No co. R		Co. R	
	4th day	9th day	4th day	9th day	5th day	9th day	5th day	9th day	5th day	9th day	5th day	9th day
<b>Asparagin</b>												
<i>Rh. meliloti</i> 101.....	52	80	1180	2000	36	40	1460	2000	16	20	1280	2000
“ “ 110.....	50	80	1040	2000	52	60	1120	2000	32	20	1060	2000
“ “ 123.....	48	80	240	2000	52	60	220	1500	14	20	280	1600
“ “ 132.....	12	20	132	1200	14	20	30	240	22	20	162	1400
<i>Rh. trifolii</i> 205.....	20	14	1760	2000	14	20	900	1800	8	0	900	2000
“ “ 206.....	14	14	1160	2000	30	20	620	2000	20	20	740	2000
“ “ 208‡.....	14	0	920	2000	12	20	400	2000	18	20	800	2000
“ “ 205.....	12	14	1860	2000	34	40	1640	2000	16	0	840	2000
<b>Potassium nitrate</b>												
<i>Rh. meliloti</i> 101.....	56	80	1160	2000	12	20	700	2000	12	20	120	1500
“ “ 110.....	54	140	1300	2000	28	60	1160	2000	20	20	500	2000
“ “ 123.....	42	60	1340	2000	6	60	1180	2000	6	20	640	2000
“ “ 132.....	32	60	380	2000	22	40	170	1600	12	20	260	1800
<i>Rh. trifolii</i> 205.....	16	20	1180	2000	20	40	780	2000	16	20	1220	2000
“ “ 206.....	22	20	1300	2000	40	60	920	2000	22	20	2000	2000
“ “ 208‡.....	26	120	720	2000	18	60	700	2000	18	40	820	2000
“ “ 205.....	30	40	940	2000	14	40	1500	2000	22	20	1120	2000

\* The figures given for the 4th and 5th day growths are microscopic counts, whereas the figures for the 9th day are estimates. In the case of the highest figures given, 2000 millions per cc., the actual numbers present are, in many instances, probably considerably higher than this figure.

† *Rh. trifolii* 205 culture obtained from University of Wisconsin; all other cultures obtained from Iowa State College.

‡ All results reported with this organism were obtained at a later date than in the case of the other organisms.

with those reported here in tables 1-3, it seemed desirable to determine whether the difference was due to the bacterial strains used. Using cultures which D. W. Thorne very kindly supplied, we carried out an experiment in which their experimental conditions (11, table 1) were duplicated fairly closely. Our usual medium, described above, was used, except that, in order to reduce the quantity of growth factor added as an impurity, only 0.2 per cent c.p. sucrose was added.

Three successive transfers were made, using 1 cc. of inoculum per 25 cc. of medium, according to their method. The first transfer was made from cultures grown on commercial sucrose medium which contained some accessory substance. In the subsequent successive transfers all inoculations were made from the corresponding flasks of the preceding series to which no growth factor had been added.

The results with seven bacterial strains obtained from Thorne, reported in table 4, are in agreement with the data in tables 1-3. These organisms made only a very slight growth on a medium containing either asparagin or potassium nitrate and adequate iron unless coenzyme R was added. This was true even though 1 cc. of inoculum was used. The growths over a 5-day period were, on the average, not greatly different with asparagin and potassium nitrate; some strains preferred one nitrogen source, and some strains preferred the other. The different results obtained by Thorne and Walker are therefore not due to strain variation.

In these and other studies not reported here it has been observed frequently that most strains of *Rh. meliloti* make larger growths on relatively small amounts of growth substance than do strains of *Rh. trifolii*. In control flasks where clover bacteria commonly show no macroscopic growth (less than 20 millions per cubic centimeter) the alfalfa organisms may show a definitely positive growth (40-80 millions per cubic centimeter). The reason for this difference has not been determined.

#### EFFECT OF VARYING CONCENTRATIONS OF COENZYME R ON GROWTH

Typical results showing the effect of different concentrations of coenzyme R on the growth of three cultures of rhizobia are given in table 5. Each flask was inoculated in duplicate. In experiment 1 two drops of inoculating culture were added to each flask, giving an initial population of approximately 600,000 organisms per cubic centimeter; in experiment 2 the initial population was about 300,000 organisms per cubic centimeter. In both experiments the media contained potassium nitrate and 0.2 per cent of a sucrose known to be fairly low in growth substance. The sample of coenzyme R used, which had been prepared from molasses, was considerably less concentrated than extracts prepared most recently from *Azotobacter* cultures.

Table 5 shows that, over the concentration range tested, the number of organisms was roughly proportional to the concentration of growth substance added. At the highest concentration of growth factor, there were usually fewer organisms per unit of coenzyme R present, as was to be expected. From the data of experiment 2 it was calculated that the control flasks actually contained coenzyme R equivalent to that in about 0.05 p.p.m. of the coenzyme R preparation added. This was, of course, added in the inoculum and in the sugar.

It appears from these and other results that a definite minimum quantity of growth substance is needed for the formation of each bacterial cell. As was

pointed out previously (2, 3, 7), respiration studies show that additions of coenzyme R at concentrations equivalent to the maximum used in table 5 commonly produce a two- to four-fold increase in respiration during the first few hours and before an increase in numbers occurs. Coenzyme R, therefore, apparently exerts its effect on growth through its initial effect on respiration.

Incidentally, it is desired to point out that the  $Q_{O_2}$  (cu. mm.  $O_2$  consumed per hour per mgm. dry weight) of rhizobia is much lower than that for many other bacterial species. Unfortunately, in a previous publication (3) it was stated that the  $Q_{O_2}$  may reach values as high as 1,000; this figure should have been given as 50. In most experiments it is less than 30.

TABLE 5  
*Effect of varying concentrations of coenzyme R on growth of rhizobia*  
(Millions of bacteria per cc.)

QUANTITY OF COENZYME R ADDED	EXPERIMENT 1				EXPERIMENT 2	
	<i>Rh. trifolii</i> 205*		<i>Rh. meliloti</i> 131*		<i>Rh. trifolii</i> 209*	
	3 days	7 days	3 days	7 days	4 days	7 days
p.p.m.						
Control	22	48	32	52	10	23
0.1	24	52	30	70	....	....
0.2	118	132	66	160	62	93
0.5	164	212	92	300	84	214
1.0	268	720	124	800	181	520
2.0	...	....	...	...	320	680
5.0	840	1280	356	820	1020	1550

\* Cultures obtained from University of Wisconsin.

#### DISCUSSION

The data reported, together with those from numerous other similar experiments not reported, confirm our previous findings that many, but not all, strains of rhizobia require coenzyme R in order to make good growths. We have not attempted to determine whether these organisms can be kept alive and growing slowly for a large number of successive transfers on media containing no accessory growth substance. It would, in fact, be difficult to perform this experiment because of the difficulty in eliminating all traces of the growth factor from the medium, and because the inoculum itself contains the substance. In our experiments we have been interested only in the conditions essential for obtaining *good* growths (500 millions or more bacteria per cubic centimeters in 4 or 5 days).

These experiments also show that iron does not act as a substitute for coenzyme R, and thus, insofar as they are comparable, confirm the conclusions of our previous (2) iron studies. Rhizobia, in contrast to *Azotobacter*, require so little iron that, in many instances, the iron impurities in the chemicals used are adequate for good growths.

The inability of reducing substances, such as thioglycollic acid and cysteine, to act as substitutes for the growth substance is again shown by the data presented here. Although it is quite possible that coenzyme R acts through the oxidation-reduction system inside the cell, we have not been able to obtain direct evidence for this view. Not only do reducing agents added to the media fail to act as substitutes for coenzyme R, but direct potentiometric measurements show that the addition to the media of our more concentrated preparations at concentrations adequate for maximum growth has essentially no effect on the  $E_h$  values of the media.<sup>2</sup>

The conclusion of Thorne and Walker (11) that "no evidence was found which indicates that the root nodule bacteria require any complex, unidentified substances for their growth" is, therefore, contrary to both our earlier and our present experience. Under the experimental conditions, 19 strains of rhizobia, including 7 supplied by Thorne, all of which are capable of making good growth on laboratory media, failed to make *good* growths unless coenzyme R was added. We do not wish to imply, however, that all rhizobia respond to additions of this growth factor. We emphasized previously that the cowpea and soybean bacteria, as well as some of the others that usually grow poorly on laboratory media, ordinarily make little response to additions of coenzyme R. Furthermore, our more recent studies show that an occasional strain of rhizobia of species other than *Rh. trifolii*, *Rh. leguminosarum*, *Rh. meliloti*, and *Rh. phaseoli*, can grow readily on laboratory media to which no coenzyme R has been added. Of 27 strains of the four species mentioned, which we have studied at various times, only 1, however, has been found to make a good growth without additions of the growth substance, and even this strain shows some response to the material. This one strain slowly synthesizes coenzyme R. Studies along this line will be reported shortly. Since strain variation among bacteria is the rule, variations with respect to need for the growth substance are not surprising.

A close study of the paper by Thorne and Walker indicates that the differences between their results and ours lie more in the interpretation of the data than in the data themselves. Although they report that good growths were repeatedly obtained, and for a large number of transfers, in a purified medium containing ammonium chloride or asparagin as a nitrogen source, they also state that "the accessory substances reported by Allison and Hoover are able to induce large increases in the growth and respiration of *Rhizobium* in media composed of highly purified materials. This stimulative effect has been noted in media with  $\text{NH}_4\text{Cl}$  or asparagin, as well as  $\text{KNO}_3$  as the source of nitrogen." Thorne and Walker therefore presented the view that coenzyme R is a non-essential, rather than an essential, growth substance. This interpretation involves the assumption that the growth they observed was not due to small quantities of growth substance, added unintentionally. On the other hand, we are strongly of the opinion that the scanty growths we obtain in the ab-

<sup>2</sup> Allison, F. E., and Minor, F. W. Unpublished results.

sence of intentionally added growth substance are due entirely to traces in the sugar and in the inocula used. If very small growths are to be obtained in such control flasks the coenzyme R in the medium must be reduced to the minimum by careful purification of all chemicals used and by inoculating with a relatively small number of organisms that have been grown on a medium low in growth factor.

A large number of empirical tests of various chemical compounds and growth factors essential for other organisms have not shown any of them to be coenzyme R. The actual chemical constitution of the substance has not been determined, but, as stressed before, there is nothing to indicate that it is a heavy metal, as suggested by Steinberg (9, p. 447). It is almost certainly an organic compound, not only because of its properties, but also because it is synthesized by various organisms. For instance, *Azotobacter* grows vigorously and synthesizes coenzyme R in a medium in which rhizobia fail to grow. If a little of this *Azotobacter* culture, or an alcohol extract of it, is added to some of the original medium, rhizobia will then grow rapidly in it.

#### SUMMARY

A total of 19 typical strains of *Rh. trifolii*, *Rh. meliloti*, *Rh. leguminosarum*, and *Rh. phaseoli* were found to require the addition of coenzyme R to the medium in order to make an appreciable growth. The experiments show that: (a) iron did not act as a substitute for the essential growth substance, (b) reducing substances, such as thioglycollic acid and cysteine, had very little effect on the growth of rhizobia either in the presence or in the absence of coenzyme R, (c) the need for accessory growth substance was equally evident whether the nitrogen source was sodium nitrate, ammonium chloride, or asparagin, and (d) the total growth of rhizobia over a limited range of concentrations (25- to 50-fold) of coenzyme R was very roughly proportional to the quantity of growth substance added, except in some instances at the higher concentrations.

These new data are in agreement with our previous results and in disagreement with the more recent report of Thorne and Walker that rhizobia do not require any complex, unidentified substances for their growth. Although an occasional strain of rhizobia can grow rapidly without the addition of coenzyme R, this fact has little bearing on the results reported either by Thorne and Walker or by us, since some of the same strains of bacteria were used in the two investigations.

The chemical nature of coenzyme R has not been determined, but it is unquestionably an organic compound. It is synthesized by many organisms and produces a marked increase in the respiration and growth of rhizobia.

#### Addendum

After this paper had been prepared for publication, the report of the investigations of R. Nilsson, G. Bjälve, and D. Burström [Über Zuwachsfaktoren bei *Bact. radicola*. *Annal. Landw. Hochsch. Schwedens* 5: 291-322 (1938)] and those of G. Bjälve and R. Nilsson [Stroh

als Nährboden für *Bact. radicola* und andere Mikroorganismen. Ibid. 71-88] appeared in print. Both papers show the inability of *Rh. trifolii* to grow in the absence of an essential growth substance. Nilsson, Bjälfve, and Burström obtained no growth on a synthetic medium with  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$ , or asparagin as the nitrogen source, but when yeast extract was added, normal growth occurred. Likewise, the addition of glyceric aldehyde, cysteine hydrochloride, or glutathione did not enable the bacteria to grow in the absence of essential growth substance. They conclude from their experiments, carried out in part for the purpose of checking the results of Thorne and Walker as well as those reported by us, that "Nur nach Zugabe von gewissen Extrakten aus nativem Material erfolgt ein Wachstum auf den synthetischen Medien."

*Note added to galley proof.* More recently P. M. West and P. W. Wilson [Synthesis of growth factors for *Rhizobium trifolii*. *Nature* 142: 397-398 (1938) and Growth-factor requirements of *Rhizobium trifolii*. *Jour. Bact.* 36: 306-307 (1938)] reported the existence of a growth-connected factor for rhizobia which, since it is thermolabile, is obviously not identical with coenzyme R.

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## BOOK REVIEWS

*Productive Farm Crops.* By E. G. MONTGOMERY. J. W. Lippincott Company, New York, 1938. Pp. viii + 521, illus. 222.

The present volume is the fifth edition of a well-known book. It is more complete than the earlier editions and has been markedly improved from the standpoint of craftsmanship.

At this particular time, producers of farm crops need more help and guidance than they ever did before in planning the production of staple agricultural commodities. The author is well aware of this situation. In the preface to the fifth edition, he says:

In the preparation of this book, the author has endeavored to develop the fundamental principles of crop production, as demonstrated by practical experience. In general the principles referred to are supported by experimental evidence. No exhaustive analysis of experimental evidence is attempted, but only sufficient to clearly prove the principles. Involved and debatable problems are generally avoided, as there is sufficient standard and accepted work for the scope of this book.

The text is intended for the use of students having some practical knowledge of crop production. It is hoped to meet the needs of students taking a general agricultural course. Being of a practical nature, the book will also be found a handy book for farmers desiring a reference book covering all agricultural crops.

The book contains 45 chapters, which are entitled respectively: Classification, Origin and Distribution of Field Crops; How Plants Grow; The Production of Seeds; Comparative Study of Cereals; Cropping Systems; Corn; Climate and Soil Required for Corn; Corn Culture; Preparation of Land for Corn; Tillage for Corn; Harvesting and Utilizing Corn; Corn Insects and Diseases; Pop-Corn and Sweet Corn; Corn Judging; Wheat; Origin and Description of Wheat Types; Wheat Culture; Harvesting, Marketing, and Utilizing Wheat; Diseases and Insect Enemies; Oats; Culture of Oats; Harvesting and Utilizing the Oat Crop; Barley; Rye; Buckwheat; Cotton; Cotton Culture; Flax; Sorghums; Irish Potatoes; Culture of Irish Potatoes; Sweet Potatoes; Classification and Distribution of Forage Crops; Characteristics of Economic Grasses and Legumes; Grass Mixtures—Seeds and Seeding; Care of Grass; The Principal Cultivated Grasses; The Secondary Grasses; Millets; Legumes; Alfalfa; The Clovers; Cow Peas, Soy Beans, Field Peas, Vetches, Peanuts; Root Crops; and Tobacco Production. There are also three appendixes and an index. The appendixes are designated, respectively: Legal Weights per Bushel of Seeds; Market Grades of Hay and Straw; and Grades of Grain.

The student, as well as the progressive farmer, will find much useful information in this book. The information will help him to orient himself as to domestic production, production in foreign countries, and export and import



markets. He will also be able to utilize this information in planning his live-stock enterprises. Moreover, the producers in different sections of the United States will gain a better perspective of the important producing areas and the distribution of crop production in the United States.

*The Chemical Analysis of Foods and Food Products.* By MORRIS B. JACOBS. D. Van Nostrand Company, Inc., New York, 1938. Pp. xx + 537, figs. 56, tables 65.

The value of foods is no longer to be measured in quantitative terms alone. Nutrition studies of many sorts have taught us that the products used in the feeding of farm animals and of humans vary widely in their composition. They vary as widely in their ability to provide for maintenance and growth. For one thing, well-informed persons attach proper importance to the content of phosphorus and calcium in foods. The so-called *minor* ingredients of plant ash are being evaluated intelligently. The place of vitamins, hormones, and of other plant constituents in nutrition is now more clearly understood. For this and other reasons, *The Chemical Analysis of Foods and Food Products* will be found useful to the laboratory technician, to the chemist, and to the dietitian.

The author was clear in his own mind as to the scope of his undertaking. He notes in his preface:

This book was written with a number of objectives. First and foremost was the desire of the author to give systematic coverage to the salient facts of the chemical analysis of foods and food products and to include certain of the newer aspects of food analysis such as the chemical assay of vitamins, the detection of improper pasteurization of milk, the homogenization of milk, the detection of gums and methods for the detection of newer types of sophistication of foods. Many important analytical procedures have been entirely neglected, not only in literature, but even by so eminent a society as the Association of Official Agricultural Chemists whose latest edition of methods, 1935-36 contains no word on the detection of improper pasteurization of milk, nor any chemical methods for the vitamins although Tillman's method for vitamin C has been recognized as adequate since 1928.

The book is made up of 17 chapters, entitled respectively: General Methods; Physical Chemical Methods; Coloring Matter in Foods; Preservatives in Foods; Metals in Foods; Milk and Cream; Milk Products; Oils and Fats; Sugar Foods and Carbohydrates; Gums, Cereals, Starch and Other Polysaccharides; Jams, Jellies, Fruits; Spices, Flavors and Condiments; Non-alcoholic Beverages and Allied Products; Alcoholic Beverages; Meat, Meat Products, Fish and Eggs; Vitamins; and Inorganic Determinations. Appendix tables cover 27 pages, and there are adequate subject and author indexes.

Altogether, the volume should prove to be a distinct aid to many persons, not least among them the technicians who are searching for new industrial uses of agricultural products.

*Physical Chemistry.* By J. N. BRÖNSTED. The Chemical Publishing Co. of New York, Inc., 1938. Pp. xv + 394, tables 30, figs. 73. Price \$5.00.

In his foreword to the book, Prof. F. G. Donnan, of the University of London, says:

An outstanding feature of this work lies in its systematic application of the thermodynamic methods of Willard Gibbs. The clarity, security and elegance of treatment thereby obtained are apparent on almost every page. For this achievement, Professor Brönsted is to be heartily congratulated.

By way of further acquainting the reader with the nature of this book, the following may be quoted from the preface to the English edition.

The present book is a translation of the author's "Laerebog i fysisk Kemi," which was published in 1936, and forms the basis for instruction in physical chemistry at Copenhagen University and the Danish Technical College.

In this text-book special emphasis is laid on the thermodynamic foundation of physico-chemical laws. The treatment employed is based upon the "thermodynamic functions" of Gibbs, since in the author's opinion this is the easiest way of attaining the combination of simplicity and rigour which should be the aim of a theoretical text-book. It is often supposed that the conception of thermodynamic functions is a difficult one, and that their use demands special powers of abstract thought. It is the author's view, however, that this is not in general the case, while even if such difficulties should occur they will be amply compensated by the uniformity of treatment and certainty of operation which characterise the methods of Gibbs.

There are altogether 11 chapters in this volume. The titles of these chapters follow: The Laws of Thermodynamics; States of Aggregation; Molecular Theory; Mixtures; The Theory of Dilute Solutions; Homogeneous Equilibria; Electrolytes; Reaction Kinetics; Electrochemistry; Affinity; and Surface and Colloid Chemistry.

It is to be regretted that a book of such fine quality is not provided with a satisfactory subject index. However, this should not lessen the merits of the author's contribution to a rapidly expanding field of chemistry.

*Agricultural Analysis.* By C. HAROLD WRIGHT. Thomas Murby & Co., London, 1938. Pp. ix + 343, figs. 8. Price 16s net.

The author is already known for his *Soil Analysis*, a handbook of physical and chemical methods. The publication of the revised edition of this work is now pending. In his *Agricultural Analysis* the author deals with methods exclusive of those used for the examination of soils.

As a laboratory manual, the present work is intended to serve students, teachers, and laboratory technicians. To quote the author:

This book is a laboratory manual giving the details of the methods of analysis of fertilizers, feeding stuffs, milk, milk products, insecticides and fungicides with reference to the sources of information. It also contains the preparation of the indicators and standard solutions used in the methods described and the data required for calculating the results. It is intended for agricultural analysts with limited library facilities, but it is hoped that it will also be of use to research workers and advanced students.

The major topics dealt with by the author are entitled, respectively: Introduction; Preparation of the Sample; Nitrogenous Fertilizers; Phosphatic

Fertilizers; Phosphate Rock; Potassic Fertilizers; Lime and Limestone; Organic Constituents of Feeding Stuffs; Mineral Constituents of Feeding Stuffs; Milk; Milk Products; Insecticides and Fungicides; and Solutions for Volumetric Analysis. There are also three appendixes (entitled: International Atomic Weights; Gravimetric Factors and their Logarithms; and Volumetric Factors and their Logarithms), and an author and subject index.

Aside from the general and popular information contained in this book, the reader will find direct and helpful reference to various official methods employed in the analysis of agricultural products.

*Guide to Eastern Ferns.* By EDGAR T. WHERRY. The Science Press Printing Company, Lancaster, Pa., 1937. Pp. iv + 220, illus. 102.

This is a most interesting little volume. The horticulturist and the professional and amateur gardener will welcome it. The descriptions of the different ferns in the eastern region will serve as a direct aid to the teacher and the student alike. In the words of the author:

This guide has been prepared to fill a need for an aid in the identification of the ferns and fern-allies of the region from Pennsylvania and New Jersey to Virginia, of convenient size for field use, and, though non-technical, free from errors and misidentifications such as occur in several current fern books. The data as to each species are presented under five headings: History; Features, especially those not brought out by the drawings; Habitat, ascertained by extensive field work; Range, as known to date; Remarks, comprising methods of distinguishing similar species, and corrections of certain errors often made in amateur writings on these plants, which, once published, get copied by one uninformed writer after another indefinitely.

Aside from the introduction, the book contains a glossary of technical terms; a classification; illustrations and descriptions of species; a discussion of fern cultivation; and an index to genera.

This book should find a place on the reference shelf of the gardener and botanist.

*Animal Nutrition.* By LEONARD A. MAYNARD. McGraw-Hill Book Company, Inc., New York and London, 1937. Pp. xiv + 483, tables 33; figs. 36. Price \$4.00.

The conversion of plant products into animal products represents one of our major economic enterprises. On the foundation built by the soil technologist and the agronomist, the geneticist has worked successfully toward the development of better and more profitable strains of livestock. But, even with the best foundation of farm animals, economic returns are not possible except as rational management and effective nutrition methods are employed.

The present work is a valuable contribution on the subject of animal feeding. In the author's own words:

Nutrition is a chemical process and its principles must be presented in chemical terms. It is assumed that the student has an elementary knowledge of organic chemistry and of physiology. The early chapters of this book provide a review and extension of this knowledge as

related to those substances and processes with which nutrition deals. These discussions are limited to the essentials of the language in which the principles of nutrition must be presented.

In the discussion of growth, reproduction, lactation, and other body functions particular attention is given to the nutritive requirements of the various species of farm animals. But the major purpose is to teach how the facts of nutrition are being learned experimentally and how they find application in practice. A consideration of the detailed feeding practices which differ for the various species lies outside the scope of this book; but the discussions here included should provide a background for a better understanding of these practices as presented in the production courses for the various species.

The book contains a preface and 16 chapters. These are entitled: The Expanding Field of Nutrition—An Introduction; The Animal Body and Its Food; Some Physical Bases of Life Processes; The Carbohydrates and Their Metabolism; The Lipids and Their Metabolism; The Proteins and Their Metabolism; The Inorganic Elements and Their Metabolism; The Vitamins; Feeding Experiments. The Determination of Digestibility; Nutritional Balances; Measures of Total Nutritive Energy; The Fasting Catabolism. Maintenance; Growth; Reproduction; Lactation; and Work Production. Both the author index and the subject index make the book more useful for reference purposes.

The teacher and the student will derive much satisfaction from this work, not alone because of the satisfactory arrangement of the material presented, but also because of the numerous references cited and the lines of thought which the reading of the book will develop.

*The Soybean Industry.* By A. A. HORVATH. The Chemical Publishing Co. of New York, Inc., 1938. Pp. vi + 221. Price \$4.00.

The two Americas owe much to the Old World for the plant material that it has contributed to our crop resources. The soybean is one of the remarkable contributions of Asia to the economic resources of North America. It came to the shores of this continent after the middle of the nineteenth century. Its economic possibilities were not appreciated at that time. The first introductions were accepted as new botanical specimens to be grown in our botanic gardens. In the course of time, the soybean became one of our important staple crops. More recently, it was recognized as a source of raw materials for nonagricultural industries. This is precisely the point of view that guided the author in the preparation of *The Soybean Industry*. In the introduction to his book, he says:

One of the most striking agricultural developments in the United States in recent times has been the rapid rise of the soybean. In 1907 there were 50,000 acres; in 1935, nearly 5,500,000. In 1920, seed production was 3,000,000 bushels; in 1935, about 40,000,000. Remarkable progress has been made in the last few years in developing food and industrial uses for the soybean, the oil, and meal. At present about 45 oil mills, including a few cottonseed oil mills, are crushing soybeans; more than 40 concerns are manufacturing soybean food products and soybean flour; and more than 75 factories are turning out various industrial products made from soybeans. Soybean oil has become an important product in many industries. In addition to the use of the meal in livestock feeds, considerable quantities are

utilized in the manufacture of foods and industrial products. As yet, however, we are only beginning to suspect the extent of the potentialities which further scientific research may discover and which commercial development may transform into actualities.

Aside from the introduction, the body of the book is made up of 20 chapters, a bibliography, a list of useful books, and an index. The chapters are designated as follows: Edible Whole Soybean Flour; Pressure Oil Milling; Oil Milling (machinery and procedures); Press Oil; Press Meal; Solvent Extractions; Safety in Solvent Extraction and in Flour Milling; Efficiency of Solvents and Their Effect on Oil Quality; Experimental (Laboratory) Extraction of Phosphatides; Commercial Extraction of Phosphatides; Soybean Oil; Refining of Soybean Oil; Blown, Sulfonated and Hydrogenated Oil; Technical Uses of Soybean Oil, Core Oil and Cutting Fluid; Phosphatides (Lecithins) and Their Uses; Soybean Protein; Industrial Protein; Plastics; Adhesives and Sizing Materials; and Solvent Extraction Meal.

To say the least, this book will help both the agronomist and the technologist to orient themselves in a rapidly expanding field. The oils, fats, and plastics derived from soybeans will become economically more important with the passing years.

*The Science and Practice of Canadian Animal Husbandry.* By J. W. G. MACEWAN AND A. H. EWEN. Thomas Nelson & Sons Limited, Toronto, Canada, 1936. Pp. xiv + 462, illus. 45.

The authors and publishers of this book are to be commended for a task well done. The paper, the printing, and the illustrations are all of fine quality; but what is more important is the presentation of the subject matter. The vast extent of Canada, its climate, and its soils have already encouraged the establishment and development of one of the great livestock enterprises of the world. There is room for much expansion. The present book may be accepted as one of the means to that end. A part of the foreword, written by James G. Gardener, may well be quoted in this connection.

The live-stock industry of our Dominion takes many forms, depending somewhat on geographic, climatic and soil conditions. Whatever the phase of live-stock production, whether it be ranching or farm production, dairying or meat production, pure bred or commercial production, it calls for the highest type of personal initiative and skill. Breeders are entrusted with the responsibility of controlling the intricate processes of heredity and hence the type and utility of farm animals, while the problems of feeding and nutrition are scarcely less complex and deserving of study. The demand for our live-stock products at home and abroad depends greatly upon the quality we are able to maintain and the skill with which our tasks are completed.

Reference may also be made to the first paragraph in the authors' preface:

Numerous inquiries received from farmers, stock men and students testify to the need for a treatise on Canadian Animal Husbandry. The following chapters represent an effort to meet that need, and in so doing to include under one cover the essential points about the theory and practice of breeding, feeding, management and related problems. It has been

the constant aim of the authors to treat the subject matter in such a manner that the book would serve as a text for students of agriculture and a guide and reference to practical live-stock breeders.

The contents of the book include a foreword, a preface, and 23 chapters grouped under seven parts. These parts are entitled, respectively: The Principles of Breeding; Breeds of Live-Stock in Canada; Principles of Nutrition; Feeds; Feeding and Management of Farm Stock; Marketing of Live-Stock; and Farm Meats. The chapters themselves are designated: Animal Genetics; Reproduction; Fertility-Sterility; Breeding Practices; Breeds of Cattle; Breeds of Sheep; Breeds of Pigs; Breeds of Horses; Physiology of Digestion; Constituents of Feeds; Feeding Standards; The Practice of Feeding; Concentrates; Pastures, Hays, Straws; Roots and Tubers; Silos and Silage; Dairy Cattle; Beef Cattle; Sheep; Pigs; Horses; Marketing of Live-Stock; and Farm Meats. There are also 7 appendixes, a bibliography, and an index.

The book will be found to be a source of useful information for the teacher, the student, and the breeder and feeder of farm animals.

*Soilless Growth of Plants.* By CARLETON ELLIS AND MILLER W. SWANEY. Reinhold Publishing Corporation, New York, 1938. Pp. 155, frontispiece, figs. 58. Price \$2.75.

It may be that the recent publicity about so-called *dirtless farming* has given the reading public an exaggerated notion about the production of plants in sand or water culture. None the less, there are two important fields that relate to the subject dealt with by the authors. One is the field of soil science: the other is that of economics.

The following paragraph, quoted from the foreword, will help the reader to understand the purpose of the authors in preparing this book:

In the past few years so great a degree of interest has been aroused in so-called soilless growth that a popular discussion of the subject seems in order. The present text was written after numerous laboratory tests and investigations had been carried out. It is hoped that this volume will prove useful to those who desire to grow plants by the methods described herein.

Reference may also be made to a paragraph from the introduction. This paragraph reads:

Like so many other practices, that of soilless growth continued practically unnoticed by the non-technical person until a very few years ago; and within recent months there has been an enormous surge of popular interest in this art of growing plants. The essential feature of the soilless method is the use of so-called "nutrient solutions," which merely consist of chemical plant food dissolved in water. A number of small water-culture gardens employing these nutrient solutions have been in operation during the past year or so, and a considerable number of greenhouse establishments are at present producing both vegetables and flowers by this method of cultivation. Soilless growth is also known as "hydroponics," aquaculture, water-culture, tray agriculture, or tank farming. When carried on in the proper manner, it enables one to obtain plants of considerably larger size than is ordinarily attained in soil. For instance, tomato vines 23 feet in height have been reported grown by soilless methods.

Aside from the foreword and the introduction, the book contains 8 chapters and an index. The chapters are entitled, respectively: Chemistry of Plant Life; Growing in Mineral Aggregates; Growing in Water; Household Plant Culture; Commercial Aspects; Special Chemicals; Common Detriments; and Nutrient Formulas.

The entire subject is a fascinating one. The average person is fond of plants. He finds joy in watching them grow. He will, no doubt, obtain added inspiration from some of the recent developments in plant production—not least among them those described by the authors.

*Annual Review of Biochemistry*, Vol. VII. JAMES MURRAY LUCK, Editor, AND CARL R. NOLLER, Associated Editor. Annual Reviews, Inc., Stanford University P. O., California, 1938. Pp. ix + 571. Price \$5.00.

The present volume is the seventh of the series. It brings up to date an account of scientific findings rich in facts and suggestions. The editors of the book have rendered and are rendering an extremely valuable service. They have been fortunate in the selection of contributors—each working in his special field.

It would be proper to quote a portion of the preface. It is noted there that

An introduction to the present volume of the Review can refer to very few matters that have not received mention in the earlier volumes. Each year, however, it is a pleasure to recall those phases of our editorial duties that bring us into association with the contributors of the reviews and with some of the readers. The cooperation of our colleagues, year by year, in preparing these reviews has been most cordial and complete, despite the vexatious restrictions and importunities with which we perennially tax their patience. Every investigator in biochemistry, impressed as he must be by the fertility of research and the wealth of literature in this expanding science, cannot but be appreciative of the difficulties that attend the labors of a reviewer—the selection of papers for review, their critical interpretation, and their integration into a coherent chapter.

It has also been satisfying and helpful to receive from time to time from the readers of the Review suggestions with respect to authorship and subject matter. It is our hope that an increasing number of our colleagues may extend to us the assistance that comes from such suggestions in order that the quality of the Review and its usefulness may steadily be enhanced.

The scope of the reviews of progress in the special field of biochemistry is best indicated in the following list of topics and of the contributors: Biological Oxidations and Reductions, by L. Michaelis and C. V. Smythe; Chemistry of the Crystalline Enzymes, by J. H. Northrop and R. M. Herriott; The Chemistry of the Carbohydrates and the Glycosides, by E. F. Armstrong; The Chemistry of the Acyclic Constituents of Natural Fats and Oils, by G. S. Jamieson; The Chemistry of Amino Acids and Proteins, by M. Bergmann and C. Niemann; The Chemistry and Metabolism of the Compounds of Phosphorus, by K. Lohmann; Carbohydrate Metabolism, by H. E. Hinwich; Fat Metabolism, by F. Verzar; Metabolism of Amino Acids and Proteins, by H. A. Krebs; The Metabolism of Creatine and Creatinine, by K. Thomas; Acid-Base Metabolism, by J. Sendroy, Jr.; The Hormones, by O.

Wintersteiner and P. E. Smith; The Vitamin-B Group, by R. A. Peters and J. R. O'Brien; Vitamin C (Ascorbic Acid, Cevitamic Acid), R. A. Peters and H. W. Davenport; The Fat-Soluble Vitamins, by J. C. Drummond; Nutrition, by H. H. Mitchell; The Biochemistry of Muscle, by E. Lundsgaard; Liver and Bile, by A. C. Ivy and L. A. Crandall, Jr.; Animal Pigments, by R. Lemberg; The Terpenes, Saponins, and Closely Related Compounds, by W. A. Jacobs and R. C. Elderfield; Organic Insecticides, by F. B. LaForge and L. N. Markwood; The Chemistry of Bacteria, by W. H. Peterson and M. J. Johnson; Growth Regulators in the Higher Plants, by P. Boysen. There are also author and subject indexes, which, for obvious reasons, occupy considerable space.

Once again, the editors have placed under obligations to themselves a large number of students, technicians, and teachers who have come to depend on them for an important and constructive service.

*Handbook of Practical Bacteriology.* Fifth Edition. By T. J. MACKIE AND J. B. MCCARTNEY. William Wood and Company, Baltimore, 1938. Pp. xi + 586.

This is the fifth edition of a very useful work. It is not easy, even for the progressive teacher, to keep abreast of the new developments in microbiology. Aside from medicine, there are the important fields of industrial and agricultural microbiology. Much reading and study are required for even a superficial review of the more recent contributions in these fields.

It is noted by the authors that

In preparing this edition we have taken the opportunity of revising those sections of the book in respect of which new knowledge and modifications in laboratory practice have necessitated review of the subject matter and the methods recommended in the previous edition. We have again endeavoured to keep the book within a given compass though it has been impossible to avoid expansion. As in the fourth edition, the subject-matter is divided into three parts; the first, general and introductory; the second, dealing with bacteriological and serological technique; and the third, describing the more important features of the pathogenic and commensal micro-organisms along with the methods of bacteriological diagnosis of the various infections. This subdivision is intended to assist the undergraduate reader who may use Part II only to a limited extent, e. g. for guidance in carrying out certain methods prescribed in an elementary practical course. As before, the text is arranged in large- and small-type matter. We trust the book will indicate to the junior worker the essentials of the subject and at the same time serve the more senior student or graduate to obtain some guidance in the actual practice of bacteriology. As in previous editions, illustrations have been purposely omitted, except a few diagrams introduced to assist in the explanation of apparatus, etc. In view of the continuous expansion of the text since the book was first published, the present edition is designated "*Handbook of Practical Bacteriology*," which seems now more appropriate than the original title.

The contents of the book are divided into three parts, two appendixes, and an index. The three parts are designated, respectively: Introductory; Bacteriological Technique; and Pathogenic Micro-organisms and Bacteriological Diagnosis. The titles of the several chapters follow: I. The General Biology of Micro-organisms; II. Immunity in Relation to Practical Bacteriology; III.



The Use of the Microscope in Bacteriology; IV. Cultivation of Micro-organisms; V. Staining Methods; VI. Animal Inoculation and Autopsy; Care of Laboratory Animals; VII. Immunological and Serological Methods as Applied to Bacteriology; VIII. Bacteriological Examination of Water and Milk; Testing of Antiseptics; Testing of Surgical Catgut for Sterility; Collection and Forwarding of Specimens for Bacteriological Examination; IX. The Pyogenic Cocci; other Pyogenic Bacteria; Pneumococcus; X. Meningococcus; Gram-Negative Cocci occurring in the Nose and Throat; Gonococcus; XI. *Bacillus Diphtheriae* and Biologically Allied Organisms; XII. The Tubercle Bacillus and other Acid-fast Bacilli; XIII. *Bacillus Mallei*; *B. Anthracis* and Biologically Allied Organisms; XIV. The Gram-Negative Aerobic Bacilli occurring as Commensals or Pathogens in the Intestine; Intestinal Protozoa; Aciduric Bacilli; XV. *Vibrio Cholerae* and Allied Organisms; *Bacillus Pestis* and *Pasteurella* Group; XVI. *Bacillus Melitensis* and *Bacillus Abortus*; Haemophilic Bacteria and Allied Organisms; XVII. *Bacillus Tetani*; Anaerobic Bacilli of Infected Wounds; *Bacillus Botulinus*; *Bacillus Chauvoei*; XVIII. Actinomyces; Other Streptothrices; Leptothrix; *Bacillus Rhusiopathiae*; Organism of Bovine Pleuropneumonia; *Bacillus Fusiformis*; *Bacillus Necrophorus*; XIX. The Pathogenic and Commensal Spirochaetes; XX. Rickettsia Group; Bartonella; XXI. The Fungi; XXII. The Malaria Plasmodia; Babesiae; Trypanosomes; Leishmaniae; XXIII. Filterable Viruses. Appendix A is called "Methods of Filtration"; and Appendix B, "Scheme of Colours for Identifying Sugar Media."

The subject matter is arranged in convenient form and will, no doubt, be appreciated by the reader.

JACOB G. LIPMAN

## AUTHOR INDEX

- Adler, S. *See* Puffeles, M.
- Ahi, S. M. *See* Bollen, W. B.
- Allison, F. E., and Minor, F. W. Coenzyme R requirements of rhizobia, 473-484.
- Asghar, A. G. *See* Puri, A. N.
- Bastiasse, E. *See* Demolon, A.
- Beater, B. E. Movement and fixation of superphosphate in soils, 453-466.
- Blair, A. W. *See* Prince, A. L., Toth, S. J., and.
- Bollen, W. B., and Ahi, S. M. Effect of "alkali" salts on general microbial function in soil, 287-306.
- Bouyoucos, G. J. Efficient and convenient type of cooling and freezing bath, 21-22; field outfit for determining moisture content of soils, 107-112; mechanical device for determining permanent wilting point of soils by cohesion method, 331-336.
- Brown, I. C. *See* Miller, J. T.
- Childs, E. C. Movement of water in heavy soils after irrigation, 95-106.
- Conn, H. J., and Darrow, M. A. Effect of moisture changes on soil as medium for bacterial growth, 365-378.
- Darrow, M. A. *See* Conn, H. J.
- Davis, L. H. *See* Seelye, F. T., Grange, L. I., and.
- Demolon, A., and Bastiasse, E. Results of lysimeter experiments, 1-8.
- Drosdoff, M., and Miles, E. F. Action of hydrogen peroxide on weathered mica, 391-396.
- Dua, A. N. *See* Puri, A. N.
- Eggleton, W. G. E. Influence of environmental factors on numbers of soil microorganisms, 351-364.
- Emmert, E. M. Rapid determination of organic carbon in soil, 397-400.
- Gilbert, B. E., and Pember, F. R. Economical uses of fertilizer elements by forage crops, 279-286.
- Grange, L. I. *See* Seelye, F. T., and Davis, L. H.
- Hilbert, G. E., Pinck, L. A., Sherman, M. S., and Tremearne, T. H. Organic phosphates: I, 409-418.
- Katznelson, H. *See* Vandecaveye, S. C.
- Keaton, C. M. Relation of soil-water ratios to pH values, 259-266.
- MacIntire, W. H., Shaw, W. M., and Robinson, B. Leaching action of rain water upon dolomite and limestone separates incorporated with quartz in outdoor lysimeters, 9-20.
- MacIntire, W. H., Shaw, W. M., Young, J. B., and Robinson, B. Behavior of calcium, magnesium, and potassium sulfates, as influenced by limestone and dolomite, 229-248.
- Miles, E. F. *See* Drosdoff, M.
- Miller, J. T., and Brown, I. C. Soils of northern and central Mexico, 427-452.
- Minor, F. W. *See* Allison, F. E.
- Mooers, C. A. Neubauer and Cunninghamella and Aspergillus niger methods for determination of fertilizer needs of soil, 211-228.
- Pember, F. R. *See* Gilbert, B. E.
- Pinck, L. A. *See* Hilbert, G. E., Sherman, M. S., and Tremearne, T. H.
- Prince, A. L., and Toth, S. J. Behavior of manganese in soils, 83-94.
- Prince, A. L., Toth, S. J., and Blair, A. W. Chemical composition of soil from cultivated land and from land abandoned to grass and weeds, 379-390.
- Puffeles, M., and Adler, S. Effect of sheep and goat manure on Mediterranean red soils, 273-278.
- Puri, A. N., and Asghar, A. G. Influence of salts and soil-water ratio on pH of soils, 249-258.
- Puri, A. N., and Dua, A. N. Hydrogen-ion activity of colloidal acids in soils, 113-128.
- Puri, A. N., and Puri, M. L. Interaction between carbonates and soils, 401-408.
- Puri, A. N., and Sarup, A. Isohydric pH value of soils, 49-56; oxidation-reduction potentials in soils, 323-330.
- Puri, A. N., and Uppal, H. L. Action of carbon dioxide on soils, 467-471.
- Puri, M. L. *See* Puri, A. N.

- Remy, Th. Fertilization in relationship to course of nutrient absorption by plants, 187-210.
- Robinson, B. *See* MacIntire, W. H., Shaw, W. M., Young, J. B., and; MacIntire, W. H., Shaw, W. M., and.
- Salmiinen, A. Titania in chemically unweathered soils, 41-48.
- Sarup, A. *See* Puri, A. N.
- Seelye, F. T., Grange, L. I., and Davis, L. H. Laterities of western Samoa, 23-32.
- Shaw, W. M. *See* MacIntire, W. H., and Robinson, B.; MacIntire, W. H., Young, J. B., and Robinson, B.
- Sherman, M. S. *See* Hilbert, G. E., Pinck, L. A., and Tremearne, T. H.
- Siderl, D. I. Formation of structure in soil: IV, 129-138; V, 267-272; VI, 337-350.
- Taylor, C. B. Bacterium globiforme in Canadian soils, 307-322.
- Toth, S. J. *See* Prince, A. L.; Prince, A. L., and Blair, A. W.
- Tremearne, T. H. *See* Hilbert, G. E., Pinck, L. A., Sherman, M. S., and.
- Uppal, H. L. *See* Puri, A. N.
- Vandecaveye, S. C., and Katznelson, H. Microbial activities in soil: IV, 57-74; V, 139-168.
- Van Itallie, T. H. Cation equilibria in plants in relation to soil, 175-186.
- Winters, E. Ferromanganiferous concretions from podzolic soils, 33-40.
- Young, J. B. *See* MacIntire, W. H., Shaw, W. M., and Robinson, B.

## SUBJECT INDEX

- Acids, colloidal, hydrogen-ion activity, 113  
 Actinomyces, number in soils, 60, 147, 293, 299, 355  
 Alkali—  
   salts, effect on microbial functions in soil, 287  
   soils, chemical properties, 295  
 Aluminum, effect on humus-clay formation, 132  
 Ammonia in soils, 157  
*Aspergillus niger*—  
   autolytic products in structure formation, 343  
   method for fertilizer requirements, 211  
 Azotobacter in soils, 67, 299  
 Bacteria—  
   cellulose-decomposing, 66  
   growth as affected by soil moisture, 365  
   nitrogen-fixing, 66  
   number in soils, 60, 146, 293, 299, 355  
*Bacterium*—  
   *globiforme*—  
     as a soil deficiency indicator, 370  
     in Canadian soils, 307  
     morphology and physiology, 313  
   *radiobacter* as an indicator for soil deficiencies, 367  
 Barley, nutrient absorption by, 191, 202  
 Base, single-base soils, action of carbon dioxide on, 469  
 Bases—  
   exchangeable, in soils treated with manure, 277  
   saturation of soil with individual, 402  
 Beets, nutrient absorption by, 202  
 Beidelite, titanium in, 45  
 Bent grass (colonial), solution culture for, 281
- 
- BOOK REVIEWS**
- Agricultural Analysis, 487-488  
 Animal Husbandry, Science and Practice of Canadian, 490-491  
 Animal Nutrition, *see* Nutrition  
 App, F., and Waller, A. G. Farm Economics, 420  
 Bacteriology, Handbook of Practical, 493-494  
 Bacteriology, Principles and Practices of, 419  
 Bakhuysen, H. L. van de S. *See* Sande-Bakhuysen, H. L. van de.  
 Bear, F. E. Theory and Practice in the Use of Fertilizers. Second edition, 173  
 Biochemistry, Annual Review of, 492-493  
 Biochemistry, Plant, 422-423  
 Biochemistry, Practical Methods in, 171  
 Biological Laboratory Technique, 77  
 Brønsted, J. N. Physical Chemistry, 486  
 Bruno, A. *See* Eckstein, O., and Turrentine, J. W.  
 Bryan, A. H., and Bryan, C. Principles and Practice of Bacteriology, 419  
 Bryan, C. *See* Bryan, A. H.  
 Bull, S., and Carroll, W. E. Principles of Feeding Farm Animals, 169  
 Carroll, W. E. *See* Bull, S.  
 Catalysis, 75-76  
 Chemical Analysis of Foods and Food Products, 486  
 Chemistry of Plant Constituents, 423-424  
 Chemistry, Physical, 486-487  
 Collingwood, C. H. Knowing Your Trees, 174  
 Cox, J. F., and Jackson, L. E. Crop Management and Soil Conservation, 78  
 Crop Management and Soil Conservation, 78-79  
 Crops, Productive Farm, 485  
 Eckstein, O., Bruno, A., and Turrentine, J. W. Potash Deficiency Symptoms, 80  
 Economics, Farm, 420-421  
 Economics of Agriculture, 77-78  
 Ellis, C., and Swaney, M. W. Soilless Growth of Plants, 490  
 Energy, World Resources, *Energiequellen der Welt*, 80-81  
 Ewen, A. H. *See* MacEwan, J. W. G.  
 Ferns, Guide to Eastern, 488  
 Fertilizers, Theory and Practice in the Use of, 173-174  
 Furnas, C. C., and Furnas, S. M. Man, Bread and Destiny, 172  
 Furnas, S. M. *See* Furnas, C. C.  
 Gatenby, J. B. Biological Laboratory Technique, 77  
 Gisvold, O., and Rogers, C. H. Chemistry of Plant Constituents, 423  
 Horvarth, A. A. Soybean Industry, 489  
 Hubbard, H. V. *See* Nolen, J.  
 Italy, soil erosion, *Le Sistemazioni Idraulico-Agrarie*, 425-426  
 Jackson, L. E. *See* Cox, J. F.  
 Jacobs, M. B. Chemical Analysis of Foods and Food Products, 486  
 Koch, F. C. Practical Methods in Biochemistry. Second edition, 171  
 Land Use, Mother Earth, 172-173  
 Land Use, Parkways and Land Values, 170-171  
 Landslides and Related Phenomena, 421-422  
 Luck, J. M., and Noller, C. R. (editors) Annual Review of Biochemistry, vol. 7, 492  
 McCartney, J. B. *See* Mackie, T. J.  
 MacEwan, J. W. G., and Ewen, A. H. Science and Practice of Canadian Animal Husbandry, 490

- Mackie, T. J., and McCartney, J. B. *Handbook of Practical Bacteriology*. Fifth edition, 493
- Maynard, L. A. *Animal Nutrition*, 488
- Millar, C. E. *Soils and Soil Management*, 420
- Montgomery, E. G. *Productive Farm Crops*, 485
- Muskat, M. *Flow of Homogeneous Fluids Through Porous Media*, 169
- Nolen, J., and Hubbard, H. V. *Parkways and Land Values*, 170
- Noller, C. R. *See* Luck, J. M.
- Nutrition, Animal, 488-489
- Nutrition, Animal, Principles of Feeding Farm Animals, 169
- Nutrition, Foundations of, 424-425
- Nutrition, Man, Bread and Destiny, 172
- Oliva, A. *Le Sistemazioni Idraulico- Agrarie*, 425
- Physics, Flow of Homogeneous Fluids Through Porous Media, 169-170
- Plant Biochemistry, 422-423
- Plant Constituents, Chemistry of, 423-424
- Potash Deficiency Symptoms, 80
- Regul, R. *Energiequellen der Welt*, 80
- Robinson, G. W. *Mother Earth*, 172
- Rogers, C. H. *See* Gisvold, O.
- Rose, M. S. *Foundations of Nutrition*. Third edition, 424
- Rothamsted Experimental Station Report for 1936, 81
- Sande-Bakhuysen, H. L. van de. *Studies on Wheat Grown Under Constant Conditions*, 75-76
- Schwab, G. M. *Catalysis*, 75
- Sharpe, C. F. S. *Landslides and Related Phenomena*, 421
- Snedecor, G. W. *Statistical Methods*, 76
- Soil Conservation, Crop Management and, 78-79
- Soil erosion, *Le Sistemazioni Idraulico- Agrarie*, 425-426
- Soil, Mother Earth, 172-173
- Soil Science Society of America, 1937 Proceedings, 426
- Soilless Growth of Plants, 491-492
- Soils and Soil Management, 420
- Soybean Industry, 489-490
- Statistical Methods, 76-77
- Swaney, M. W. *See* Ellis, C.
- Tottingham, W. E. *Plant Biochemistry*. Revised edition, 422
- Trees, Knowing Your, 174
- Turrentine, J. W. *See* Eckstein, O., Bruno, A., and Van der Post, A. P. *Economics of Agriculture*, 77
- Waller, A. G. *See* App, F.
- Wheat, Studies on Wheat Grown Under Constant Conditions, 75
- Wherry, E. T. *Guide to Eastern Ferns*, 488
- Wright, C. H. *Agricultural Analysis*, 487
- Calcium—**  
 absorption by plants, 189  
 carbonate reaction with soil acidoids, 405  
 content of various soil fractions, 5  
 exchangeable—  
   in cultivated and uncultivated soils, 387  
   in hydrogen soils treated with calcium carbonate, 406  
 relation to calcium concentration in plants, 179
- Calcium—(continued)**  
 magnesium ratio in leachings, 237  
 outgo from soils, 3, 12, 233  
 soil—  
   effect of carbon dioxide on, 469  
   influence on pH value of calcium carbonate suspensions, 407  
   reaction with sodium carbonate, 403  
 sulfate—  
   in leachings, 18  
   in soil as influenced by limestone, 229
- Carbon—**  
 dioxide—  
   action on soils, 467  
   evolution from soils, 142, 291, 296  
   sulfur, effect on evolution of, 300  
 nitrogen—  
   ratio in soils treated with manure, 276  
   relationships in soils treated with organic matter, 145
- Cation—**  
 distribution in soils, with depth, 385  
 equilibria in plants, 175  
 exchangeable, relation to absorption by plants, 178  
 saturation of soils, 249
- Clay—**  
 colloids, examination, 6  
 composition of, from granites, 5  
 fraction in laterites, 28  
 humus formations, 129  
 hydroxides of iron and aluminum, 133  
 minerals, titanium in, 45  
 sand formations, 129  
 sodium, behavior, 135  
 structure, 338
- Climate, effect on microbial activity, 64**
- Colloids—**  
 acids in, hydrogen-ion activity of, 113  
 clay, 6  
 composition of, from Mexican soils, 437
- Crops—**  
 forage, fertilizers used by, 279  
 removal of nutrients by, 202
- Dickite, titanium in, 45**
- Dilatometer, cooling bath for, 21**
- Dolomite, leaching action of water on, 9**
- Drainage, cropped and uncropped soils affecting, 2; see also Water, Lysimeter**
- Fertilization—**  
 relation to nutrient absorption by plants, 187  
 with organic phosphates, 417

**Fertilizers—**

- Aspergillus niger* method for need of, 211
- efficient use of, 201
- influence on structure, 343
- Neubauer method for need of, 211
- organic phosphate versus inorganic as, 417
- plant groups, requirements, 205
- rapid tests for need of, 226
- soil needs for, methods of determining, 211
- use by forage crops, 279

Fungi, number in soils, 60, 149, 293, 299, 355

**Granite—**

- analyses, 5
- weathering, 4, 391

Gypsum, effect on moisture profile, 99, 100, 101

**Hydrogen-ion—**

- activity of colloidal acids, 113
- concentration (pH)—
  - exchange neutrality, 49
  - isohydric, 49
  - methods of determining, 54
  - of cultivated and uncultivated soils, 387
  - relation to Eh, 158, 325
- concentration (pH), as affected by—
  - carbon dioxide, 467
  - salts, 251, 467
  - soil-water ratio, 250, 259
- concentration (pH), effect on—
  - phosphate fixation, 414
  - sugar inversion, 124

Hydrogen peroxide, action on mica, 391

**Humus—**

- clay formations, 129
- in clay-humus mixture, 341
- presence in sodium-saturated soils, 341

**Iron—**

- effect on humus-clay formations, 132
- ferric and ferrous, in soil as affected by pH, 325

Isohydric pH value of soils, 49

**Kaolinite—**

- saturation with sodium, 133
- titanium in, 45

**Laterites—**

- profile description, 23
- Samoa, 23
- use of term, 29

**Lime—**

- effect on—
  - manganese in soils, 89
  - sulfates of calcium, magnesium, and potassium, 229

**Lime—(continued)**

- Neubauer and *Aspergillus niger* tests, as affected by, 222

**Limestone—**

- dolomitic, effect on behavior of sulfates of calcium, magnesium, and potassium, 229
- leaching action of water on, 9
- state of division, importance, 18

**Lysimeter—**

- experiments, 1, 9
- leachings, analyses, 6, 11
- studies, 229

**Magnesium—**

- absorption by plants, 189
- exchangeable—
  - in cultivated and uncultivated soils, 387
  - relation to concentration in plants, 179
- in soil fractions, 5
- outgo from soil, 3, 14, 235
- soil, effect of carbon dioxide on, 469
- sulfate in soil, influence of limestone on, 229

**Manganese—**

- exchangeable, 90
- in soils, 83

**Manure—**

- effect on red soils, 273
- sheep and goat analyses, 274

Mica, hydrogen peroxide action on, 391

**Microorganisms—**

- activity—
  - organic matter transformations and, 139
  - seasonal variations in, 59
- carbon-dioxide formation and numbers of, 143
- climatic effect on, 64
- environmental effects on numbers of, 351
- humus effects, 67
- oxidation-reduction potential effects, 67, 151
- phosphate fixation by, 417
- rhythmical behavior, 360
- seasonal variation in numbers of, other than bacteria, 359
- soil types and, 57
- vegetation cover effect, 64

Minerals, loss from soils, 3

**Moisture—**

- content, method of determining, 107
- effect on pH, 250, 259
- gypsum, effect on, movement, 103
- in goat and sheep manure 274
- profiles, 98

- Montmorillonite, titanium in, 45
- Neubauer method for fertilizer requirements, 211
- Nitrate—  
formation, effect of straw on, 4  
in soils, 157
- Nitrogen—  
absorption by plants, 189, 202  
fixing bacteria, 66  
fractions in soils, 153  
gain in uncultivated soils, 382  
in goat and sheep manure, 274  
loss from soils, 3
- Nontronite, titanium in, 45
- Organic—  
carbon, method of determining, 397  
matter—*see also* Humus  
decomposition as affected by salts, 290  
fractionations, 151  
gain in uncultivated soils, 381  
loss from grass versus forest vegetation, 163  
transformations and microbial activity, 139  
phosphates, fixation studies, 409
- Peas, nutrient absorption by, 191, 202
- Phosphates—  
availability of several sources, 225  
citric-soluble, in soils, 462  
fixation in soils, 453  
loss by erosion, 465  
movement in soils, 457  
organic, studies in fixation, 409
- Phosphorus—  
absorption by plants, 189, 202  
availability, analysis of methods, 218  
distribution in soil leachings, 412  
in goat and sheep manure, 274  
loss from soils, 3
- Plant—  
groups, methods of fertilizing, 205  
nutrients—  
absorption during growth, 188  
available, comparison of methods, 215  
daily absorption, 203  
quantity absorbed, 202  
seasonal absorption, 192
- Plants—  
cation equilibria in, 175  
effect on *Bacterium globiforme*, 317  
nutrient absorption by, 187, 202  
Podzolic soils, concretions in, 33
- Potassium—  
absorption by plants, 189, 202  
availability, analysis of methods, 219  
exchangeable—  
in cultivated and uncultivated soils, 387  
relation to concentration in plants, 180  
in goat and sheep manure, 274  
outgo from soils, 3, 238  
soil, effect of carbon dioxide on, 469  
sulfate in soils as influenced by limestone, 229
- Potatoes, nutrient absorption by, 191, 202
- Rainfall map of parts of Mexico, 429
- Rape, nutrient absorption by, 191, 202
- Redtop, solution cultures for, 281
- Rhizobia—  
coenzyme R requirements, 473  
species and strains, 478
- Root distribution in soils, 70
- Rye—  
Italian, cation content, 177  
nutrient absorption by, 188, 202
- Samoa, laterites in western, 23
- Sodium—  
carbonate, reaction with—  
calcium soils, 403  
soil acidoid, 402  
exchangeable, relation to concentration in plants, 180  
soil—  
effect of carbon dioxide on, 469  
influence on pH of calcium carbonate suspensions, 407
- Soil—  
acidoid reaction with—  
calcium carbonate, 404  
sodium carbonate, 402  
calcium soil, reaction with sodium carbonate, 403  
cation equilibria in plants in relation to, 175  
chemical composition of, cultivated and uncultivated, 379  
concretions, 33  
constituents, distribution with depth, 384  
cropped and uncropped, effect on leaching, 2  
erosion, loss of phosphates by, 465  
fertilizer needs, methods of determining, 211  
fractions, variation in composition, 5  
microbial activity in, 57

## Soil—(continued)

moisture, changes affecting bacteria, 365;  
 see also Moisture, Water  
 organic carbon in, rapid determination,  
 397

## profiles—

Agua Neuva sandy loam, 439  
 concretions in, 37  
 description of a number of, 23  
 gray desert, 430  
 Irapuato clay loam, 442  
 Juarez clay, 439  
 Queretaro clay, 441  
 Tamazunchale clay, 445

## processes, 27

## rapid tests, 226

## ratings for fertilizer requirements, 220

reaction, effect of potassium chloride on,  
 255; see also Hydrogen-ion.

saline, microbial activity in, 294

series, analyses, descriptions, or experi-  
 ments with—

Agua Neuva, 439; Alderwood, 261; Ava,  
 36; Barnes, 261; Cashmere, 261;  
 Cecil, 89, 410; Chehalis, 261; Col-  
 bert, 213; Collington, 86; Colts  
 Neck, 86, 89; Cumberland, 212;  
 Decatur, 212; Denny, 38; Ephrata,  
 261; Everett, 261; Felida, 261;  
 Fullerton, 212; Garrison, 261;  
 Greenville, 261; Grundy, 38; Hart-  
 sells, 213; Helmer, 57, 69, 139;  
 Hesson, 261; Hoquiam, 261; Hous-  
 ton, 261; Huntington, 212; Ira-  
 puato, 442; Juarez, 439; Lakewood,  
 261; Las Vegas, 411; Lynden, 261;  
 Magia, 24, 26; Malatula, 25, 26;  
 Melbourne, 261; Memphis, 211;  
 Mericourt, 213; Mohave, 261;  
 Montevallo, 213; Norfolk, 410;  
 Olympic, 261; Palouse, 57, 69, 139,  
 261; Penn, 90; Phillips, 447; Ply-  
 mouth, 369; Puget, 261; Putnam,  
 38; Queretaro, 441; Ritzville, 261;  
 Rushville, 38; Saleimoa, 24, 26;  
 Salkum, 261; Sassafra, 86, 89;  
 Sharkey, 89; Spanaway, 261; Ta-  
 mazunchale, 445; Tiavi, 25, 26;  
 Torreon, \*430; Tuasivi, 25, 26;  
 Vaitele, 24, 26; Volusia, 369;  
 Walla Walla, 261; Willamette, 290;  
 Wynoose, 37

## Soil—(continued)

## structure—

autolytic products of *A. niger* in, 343  
 formation, 129, 267, 337  
 microscopic investigation of, 337

## types—

fixation of organic phosphates by, 409  
 microflora in, 57  
 water ratio, influence on pH, 249, 259; see  
 also Water, Moisture  
 zonal types, microflora, 57

## Soils—

acids in colloids of, 113

## alkali—

chemical properties, 295  
 reclamation effects of carbon dioxide,  
 469

alkaline, pH value, 55

buffer capacity, 55

Canadian, *Bacterium globiforme* in, 307

carbon dioxide evolution from, 142, 296

carbonates and, interaction between, 401

cation-saturated, studies, 177

chemical analyses of Mexican, 434

chernozem, in Mexico, 441

concretions in podzolic, 33

cultivated versus uncultivated, 379

fallow, effect on leaching, 3

ferromanganiferous concretions in, 33

fertilizer needs of, tests used, 211

flocculation of, effect of carbon dioxide on,  
 470

gain and loss of organic matter in, 382

gray desert, 428

hydrolysis of acetate by, 116, 120

Illinois, ferromanganiferous concretions  
 in, 34

intrazonal, in Mexico, 433

isohydric pH value, 49

lateritic, in Mexico, 444

laterite, see Laterites

manganese in, 83

mechanical analyses, effect of hydrogen  
 peroxide, 393

Mexico, 427

microbial activities in, 57, 139, 287

nutrient deficiencies in, indicator for, 367

oxidation-reduction potentials in, 323

Palestine, 274

phosphate fixation in, 453

podzolic and alpine meadow, 446

red Mediterranean, 273



Soils—(*continued*)

- root distribution in, 70
- salts, influence on pH, 249
- Samoa, 23
- single-base, action of carbon dioxide on, 468
- solonchak, 433, 440
- sucrose inversion by, 121, 126
- unsaturation, 387
- unweathered, titanium in, 41
- water movement in irrigated, 95
- wilting point, method, 331

Solution cultures, growing timothy, redtop, and bent grass in, 281

Straw, effect on nitrates, 4

Sucrose, inversion by soils, 121, 124

Sulfates, outgo from soil as influenced by lime, 232

## Sulfur—

- loss from soils, 3
- sulfate, outgo from soils, 243

Timothy, solution cultures for, 281

## Titanium—

- accumulation in colloids, 7
- distribution in clay fraction, 44
- in laterites, 26
- in minerals, 45
- in unweathered soils, 41

Vermiculite, alteration by hydrogen peroxide, 391

## Water—

- evaporation from cropped and uncropped soil, 2
- extract, composition of soil, 292
- leaching action on dolomite and limestone, 9
- loss from soil, 1
- movement in soils upon irrigation, 95

## Weathering—

- granite, 4
- mica, 391

Wilting point of soils, method of determining, 331





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